XII   Miscellaneous compounds and complexes

XII.1   Ternary and polynary oxides

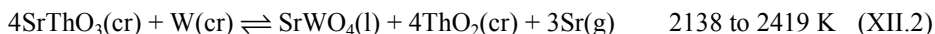### XII.1.1   Thorium - Group 2 compounds

XII.1.1.1   Strontium thorate, $SrThO_3$(cr)

The early identification of $SrThO_3$(cr) by Naray-Szabo [1947NAR] has been questioned (see discussion below), but Purohit *et al.* [2000PUR/TYA] have suggested that it is formed by combustion of a sol-gel containing $Th(NO_3)_4$, $Sr(NO_3)$ and citric acid. They indicate that its structure is a monoclinic distortion of the ideal perovskite lattice, with $a = (6.319 \pm 0.004)$ Å, $b = (3.240 \pm 0.001)$ Å and $c = (4.928 \pm 0.003)$ Å, $\beta = (117.38 \pm 0.05)°$. The only thermodynamic data for $SrThO_3$(cr) are measurements by Ali (Basu) *et al.* [2001ALI/MIS] of the pressure of Sr(g) obtained by heating $SrThO_3$(cr) in a tungsten cell from 1677 to 2419 K by weight-loss Knudsen effusion. X-ray examination of the residue after partial decomposition showed that the condensed phases were different in different temperature ranges. As well as $SrThO_3$(cr), W(cr) and ThO_2(cr), the tungstate Sr_2WO_5(cr) was present from 1677 to 2047 K, but $SrWO_4$(cr) was found in experiments from 2138 to 2419 K. Since $SrWO_4$ would be molten at these higher temperatures, Energy Dispersive X-ray analysis was carried out to determine whether there was any solubility of thorium species in this melt. Less than 10% ThO_2 was detected, but it was not clear whether this was due to dissolution of *e.g.* of $SrThO_3$ or from interference from neighbouring ThO_2 particles. Thus $SrWO_4$(l) was treated as a pure phase in the subsequent analysis, as was ThO_2(cr), although the solubility of SrO in ThO_2(cr) at 2273 K is reported to be as high as 13 mol%. The error from these assumptions was estimated by the authors to be 2.6 kJ·mol^{-1}. The authors discuss and dismiss the possible loss of oxygen to form phases such $SrWO_3$(cr) containing lower-valent tungsten.

The relevant reactions were thus assumed to be:

$$5SrThO_3(cr) + W(cr) \rightleftharpoons Sr_2WO_5(cr) + 5ThO_2(cr) + 3Sr(g) \quad \text{1677 to 2047 K} \quad \text{(XII.1)}$$

and

$$4SrThO_3(cr) + W(cr) \rightleftharpoons SrWO_4(l) + 4ThO_2(cr) + 3Sr(g) \quad \text{2138 to 2419 K} \quad \text{(XII.2)}$$

Measurements were also made below 1670 K, but the establishment of the equilibrium (probably with Sr_3WO_6(cr)) was too slow for the results to be reliable.

These measurements are analysed in detail in Appendix A. It was necessary to extrapolate the auxiliary data for the Gibbs energy of formation of the strontium tungstates from the measurement range (*ca.* 1100−1500 K) very considerably to the experimental temperature range, introducing further uncertainty into the analysis.

As discussed in Appendix A, these results correspond to a Gibbs energy of the formation reaction from the binary oxides:

$$SrO(cr) + ThO_2(cr) \rightleftharpoons SrThO_3(cr) \qquad\qquad (XII.3)$$
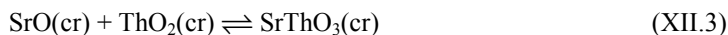
given by the equations:

$$[\Delta_r G_m]_{1670K}^{2040K} (XII.3) = -3955 - 1.300\,T \quad J \cdot mol^{-1} \qquad \text{from Reaction (XII.1)}$$

and

$$[\Delta_r G_m]_{2135K}^{2420K} (XII.3) = -17583 + 4.033\,T \quad J \cdot mol^{-1} \qquad \text{from Reaction (XII.2)}$$

Considering the extrapolations involved, and the uncertain activities, especially for Reaction (XII.2), it is not surprising that the enthalpy and entropy values differ somewhat. However, the Gibbs energies of the formation reaction from the oxides at the intermediate temperature 2100 K, $-(6.7 \pm 4.0)$ and $-(9.1 \pm 10.0)$ kJ·mol^{-1} agree remarkably well. The uncertainties are those estimated by the authors.

The SrThO$_3$(cr) phase has a lower stability than BaThO$_3$(cr), as expected, but its enthalpy of formation is much more negative than the trends in the actinide(IV) mixed oxides would suggest. Indeed [1993FUG/HAI] estimated $\Delta_r H_m$ ((XII.3), 298.15K) to be (20.0 ± 8.5) kJ·mol^{-1}, and Smith and Welch [1960SMI/WEL] were unable to prepare SrThO$_3$ by heating a mixture of ThO$_2$(cr) and SrCO$_3$(cr) in air at 1273 to 1923 K. These authors suggested that the XRD pattern attributed to SrThO$_3$(cr) by [1947NAR] fitted better to the two components SrO(cr) and ThO$_2$(cr). Similarly, Smith and Welch indicated that the diffraction pattern given by [1947NAR] for his reported CaThO$_3$(cr) agrees well with that for a mixture of ThO$_2$ and hydrated lime. Keller [1976KEL] has also thrown doubt on some of the results of [1947NAR]. Although the sol-gel technique used by [2000PUR/TYA] and [2001ALI/MIS] provides intermediate products of much smaller particle size, and thus higher reactivity that could favour the completeness of the synthesis, we note that no detailed analyses to confirm the positive identification of the final product as SrThO$_3$(cr) were made in either of these papers.

The data from Reaction (XII.1) are the less uncertain; these correspond to the Gibbs energy of formation from the elements: $[\Delta_f G_m]_{1670K}^{2040K}$ (SrThO$_3$, cr, T) $= -194680 + 36.23\,T$, where the standard state for strontium in this temperature range is Sr(g). However, owing to the uncertainties in the assessment noted above and in Appendix A and in the identification of SrThO$_3$(cr), these data are given for information only.

XII.1.1.2   Barium thorate, BaThO$_3$(cr)

BaThO$_3$(cr) is the only known ternary oxide in the BaO$-$ThO$_2$ system. Its structure is a distortion of the perovskite structure, but its diffraction pattern has been interpreted in various ways. Both Nakamura [1974NAK], in his detailed study, and Purohit *et al.* [2000PUR/TYA] describe it as an orthorhombic structure with $a = (6.345 \pm 0.002)$ Å, $b = (6.376 \pm 0.002)$ Å and $c = (8.992 \pm 0.002)$ Å, [1974NAK] with four

pseudomonoclinic units ($a' = c' = 4.498$ Å, $b' = 4.496$ Å, $\beta' = 90.28°$). Smith and Welch [1960SMI/WEL], however, attributed the faint lines additional to those from the simple cubic cell to a larger cubic cell with a doubled parameter, $a = 8.895$ Å, while Bharadwaj *et al.* [1999BHA/MIS] noted that the diffraction pattern in their samples corresponded to a simple pseudo-cubic cell with $a = 4.499$ Å.

There are no low-temperature heat capacity measurements, but Venkata Krishnan *et al.* [2001VEN/NAG] have measured the heat capacity by a DSC technique from *ca.* 320 to 820 K. They fitted their results to the expression:

$$[C_{p,\text{m}}]_{320\text{K}}^{820\text{K}} (\text{BaThO}_3, \text{cr}, T) = 137.9046 + 5.272 \times 10^{-2} T - 2.432487 \times 10^{6} T^{-2} \text{ J·K}^{-1}\text{·mol}^{-1}$$

However, as noted in Appendix A, this corresponds to a large $\Delta_\text{r} C_{p,\text{m}}$ of the formation reaction from the solid oxides in the range of temperature measurement; the calculated values are 20.0 J·K^{-1}·mol^{-1} at 320 K and 50.9 J·K^{-1}·mol^{-1} at 820 K. These large values must throw doubt on the validity of the results and these data are mentioned for information only, and have not been used to process the Gibbs energy data discussed below.

There are no experimental data for enthalpy of formation of BaThO$_3$(cr), but there are two measurements of the Gibbs energy of formation of BaThO$_3$(cr). Mishra *et al.* [1999MIS/ALI] have studied the decomposition pressure of BaO(g) from the reaction BaThO$_3$(cr) $\rightleftharpoons$ ThO$_2$(cr) + BaO(g) by Knudsen effusion from 1770 to 2136 K. As discussed in Appendix A, these results correspond to a Gibbs energy of the formation reaction from the binary oxides:

$$\text{BaO(cr) + ThO}_2\text{(cr)} \rightarrow \text{BaThO}_3\text{(cr)} \tag{XII.4}$$
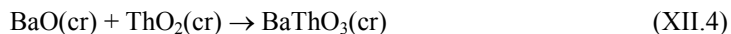
given by the equation:

$$[\Delta_\text{r} G_\text{m}]_{1770\text{K}}^{2136\text{K}} (\text{XII.4}) = -21420 - 3.058\,T \quad \text{J·mol}^{-1}$$

where the auxiliary data for the vapour pressure of pure BaO(cr) are taken from the data in [1994GUR/VEY] – see Appendix A. The small value of the entropy change of this all-solid reaction gives confidence in the experimental results. The estimated uncertainty in these Gibbs energy values is 6.0 kJ·mol^{-1}, since the uncertainty in $\Delta_\text{sub} H_\text{m}$ (BaO, g, 298.15 K) is 3.0 kJ·mol^{-1} [1994GUR/VEY].

Bharadwaj *et al.* [1999BHA/MIS] have studied the pressure of Ba(OH)$_2$(g) from the reaction BaThO$_3$(cr) + H$_2$O(g) $\rightleftharpoons$ ThO$_2$(cr) + Ba(OH)$_2$(g) from 1548 to 1683 K by transpiration in various pressures of water vapour. As discussed in Appendix A, these results correspond to a Gibbs energy of the formation reaction from the binary oxides (Equation (XII.4)), given by the equation:

$$[\Delta_\text{r} G_\text{m}]_{1548\text{K}}^{1683\text{K}} (\text{XII.4}) = -29214 + 3.574\,T \quad \text{J·mol}^{-1}$$

where the auxiliary data for the reaction BaO(cr) + H$_2$O(g) $\rightleftharpoons$ Ba(OH)$_2$(g) are taken from a recent study by [2001ALI/MIS2] using the same apparatus as [1999BHA/MIS]

((see Appendix A. However, there is a large uncertainty $(-20 \text{ kJ·mol}^{-1})$ in the range of values of $\Delta_f H_m (\text{Ba(OH)}_2, \text{g}, 298.15 \text{ K})$ from other determinations, so we estimate the overall uncertainty in the above equation to be the same.

The temperature ranges of the two studies by [1999MIS/ALI] and [1999BHA/MIS] do not, in fact quite overlap, but at 1700 K, the respective values for the $\Delta_r G_m$ ((XII.4)) are $-(26.6 \pm 6.0) \text{ kJ·mol}^{-1}$ and $-(23.1 \pm 20.0) \text{ kJ·mol}^{-1}$, and thus in reasonable agreement, although the small derived entropies of reaction are of opposite sign.

These values of $\Delta_r G_m$ (XII.4) are consistent with two estimates of the enthalpy of the formation reaction from the oxides at 298.15 K by [1983WIL/MOR] and [1993FUG/HAI]. Based on relationships between experimental enthalpies of formation of M(II)M'O3 perovskites and M' ionic radii, (M' = Ti, Mo, Hf, Zr, Tb, Pr, Ce, and U), Williams *et al.* [1983WIL/MOR] estimated $\Delta_r H_m$ ((XII.4), 298.15 K) $= -20 \text{ kJ·mol}^{-1}$ while Fuger *et al.* [1993FUG/HAI] suggested $-(31.0 \pm 8.5) \text{ kJ·mol}^{-1}$ for the same reaction, based on a larger number of experimental results, especially on actinides. Since the entropy of Reaction (XII.4) will be small, the values of this Gibbs energy at higher temperatures should not be greatly different from the standard enthalpy of reaction.

The only value selected is the weighted mean of the two consistent values of $\Delta_r G_m$ (XII.4),*viz.*

$$\Delta_r G_m ((\text{XII.4}), 1700 \text{ K}) = -(26.3 \pm 5.7) \text{ kJ·mol}^{-1}$$

The corresponding Gibbs energy of formation from the elements is then:

$$\Delta_f G_m (\text{BaThO}_3, \text{cr}, 1700 \text{ K}) = -(1320.5 \pm 7.1) \text{ kJ·mol}^{-1}$$

the reference state for barium being Ba(l) at this temperature.

Because of the doubt expressed above in the $C_{p,m}$ data of BaThO$_3$(cr), especially the extrapolation to high temperatures, we have not processed the Gibbs energies data to derive values at 298.15 K.

## XII.1.2 Thorium - Group 1 compounds

XII.1.2.1   Rubidium thorate, Rb$_2$ThO$_3$(cr)

Rb$_2$ThO$_3$(cr) is the only known ternary oxide in the Rb$_2$O-ThO$_2$ system. Hoppe and Seeger [1970HOP/SEE] reported the existence of a hexagonal structure for this compound, with $a = 3.75$ Å, $c = 19.7$ Å, Rb$_2$PbO$_3$ type and, more recently, the same group [1977BRU/HOP], reported a cubic modification, NaCl type, with $a = (5.475 \pm 0.005)$ Å, isomorphous with Cs$_2$ThO$_3$. The only thermodynamic data on Rb$_2$ThO$_3$(cr) derive from a study by Dash *et al.* [2005DAS/SIN] of the pressure of CO$_2$(g) in the reaction:

$$ThO_2(cr) + Rb_2CO_3(cr) \rightleftharpoons Rb_2ThO_3(cr) + CO_2(g) \qquad \text{(XII.5)}$$

from 952 to 1098 K by a manometric technique.

The calculated decomposition pressures from ten experimental points are well represented by the equation $\log_{10} p_{CO_2} / \text{bar} = -13031/T + 8.915$. The Gibbs energy of the above reaction is thus $\Delta_r G_m (\text{XII.5}) = 249476 - 170.680\,T$ (J·mol^{-1}). The Gibbs energy of the reaction $Rb_2O(l) + CO_2(g) \rightleftharpoons Rb_2CO_3(cr)$ over the experimental temperature range is given by $-413796 + 173.100\,T$ (J·mol^{-1}); where the data are taken from [1982GLU/GUR], adjusted to 1 bar standard state. The Gibbs energy of the formation reaction of $Rb_2ThO_3(cr)$ from the component oxides is thus:

$$Rb_2O(l) + ThO_2(cr) \rightarrow Rb_2ThO_3(cr) \qquad \text{(XII.6)}$$
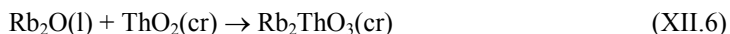
$$[\Delta_r G_m]_{952K}^{1058K} ((\text{XII.6}), T) = -164320 + 2.420\,T \text{ J·mol}^{-1}$$

Since the enthalpy of fusion of Rb_2O at 778 K is 20.0 kJ·mol^{-1} [1982GLU/GUR], the Gibbs energy change for the metastable reaction involving $Rb_2O(cr)$ would be approximately $-144320 - 23.287\,T$ (J·mol^{-1}), with an appreciable positive entropy change. Combination of the values for Reaction (XII.6) with the values for $\Delta_f G_m^\circ (Rb_2O, l)$ from [1982GLU/GUR] and $\Delta_f G_m^\circ (ThO_2, cr)$ (this review) gives finally for the Gibbs energy of the formation reactions:

$$2Rb(l) + Th(cr) + 1.5O_2(g) \rightarrow Rb_2ThO_3(cr) \qquad \text{(XII.7)}$$
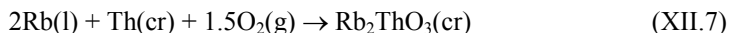
$$[\Delta_r G_m]_{952K}^{1058K} ((\text{XII.7}) T) = -1688657 + 276.470\,T \text{ J·mol}^{-1}$$

and

$$2Rb(g) + Th(cr) + 1.5O_2(g) \rightarrow Rb_2ThO_3(cr) \qquad \text{(XII.8)}$$
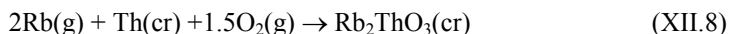
$$[\Delta_r G_m]_{952K}^{1058K} ((\text{XII.8}), T) = -1831523 + 424.248\,T \text{ J·mol}^{-1}$$

Both these equations are given since the pressure of Rb(g) over Rb(l) reaches 1 bar at *ca.* 967 K. The uncertainty in these values is estimated to be at least 11 kJ·mol^{-1}, mainly from the uncertainty in $\Delta_f H_m^\circ (Rb_2O, cr, 298.15\ K)$ which is given as 8 kJ·mol^{-1} by [1982GLU/GUR]. These expressions correspond to a very negative value for the Gibbs energy of formation of Rb_2ThO_3, in comparison with the results reported below (XII.1.2.2) for Cs_2ThO_3.

Since there are no other thermodynamic data for $Rb_2ThO_3(cr)$, no further processing of these results is possible, and no values are selected for the review.

XII.1.2.2 Caesium thorate, $Cs_2ThO_3(cr)$

$Cs_2ThO_3(cr)$ is the only known ternary oxide in the Cs_2O-ThO_2 system, and has been reported [1977BRU/HOP] as cubic, NaCl type, with $a = 5.704$ Å, isomorphous with the cubic form of Rb_2ThO_3.

The only thermodynamic data on $Cs_2ThO_3(cr)$ derive from a study by Ali (Basu) *et al.* [2000ALI/MIS] of the decomposition pressure of $Cs_2ThO_3(cr)$ according to the reaction:

$$Cs_2ThO_3(cr) \rightleftharpoons ThO_2(cr) + Cs_2O(g) \tag{XII.9}$$
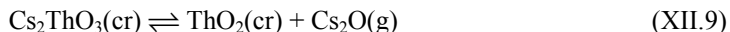
from 1100 to 1254 K by weight-loss Knudsen effusion.

X-ray diffraction on partially evaporated samples showed them to be a mixture of $Cs_2ThO_3(cr)$ and $ThO_2(cr)$ as anticipated. The thermodynamic data for the Cs-O system indicate that there are quite negligible amounts of species other than $Cs_2O(g)$ in the vapour under the experimental conditions. The calculated decomposition pressures from ten experimental points are well represented by the equation $\log_{10} p_{Cs_2O} / bar = -13942/T + 6.939$. The Gibbs energy of the above reaction is thus $\Delta_r G_m ((XII.9), T) = 266916 - 132.842\, T$ (J·mol^{-1}). The Gibbs energy of the vaporisation of $Cs_2O(l)$ over the experimental temperature range is given by $152692 - 107.587\, T$ (J·mol^{-1}); where the data are taken from the equilibrium constant given in [1982GLU/GUR], adjusted to 1 bar standard state. The Gibbs energy of the formation reaction of $Cs_2ThO_3(cr)$ from the component oxides is thus:

$$Cs_2O(l) + ThO_2(cr) \rightarrow Cs_2ThO_3(cr) \tag{XII.10}$$
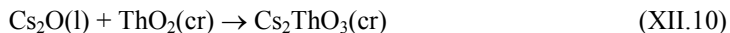
$$[\Delta_r G_m]^{1254K}_{1100K} ((XII.10), T) = -114224 + 25.254\, T \text{ J·mol}^{-1}$$

Since the entropy of fusion of Cs_2O is 26.042 J·mol^{-1}·K^{-1}, the entropy change for the metastable reaction involving $Cs_2O(cr)$ would be close to zero, which gives confidence in the experimental results. Combination of the values in the above equation with the values for $\Delta_f G_m^o (Cs_2O, l)$ [1982GLU/GUR] and $\Delta_f G_m^o (ThO_2, cr)$ (this review) gives finally:

$$[\Delta_f G_m]^{1254K}_{1100K} (Cs_2ThO_3, cr, T) = -1780323 + 441.26\, T \text{ J·mol}^{-1}$$

where the standard state for Cs is Cs(g) in this temperature range. The uncertainty in these values is estimated to be at least 20 kJ·mol^{-1}, mainly from the uncertainty in $\Delta_f H_m^o (Cs_2O, g, 298.15 K)$ which is given as 15 kJ·mol^{-1} by [1982GLU/GUR].

Since there are no other thermodynamic data for $Cs_2ThO_3(cr)$, no further processing of these results is possible, and no values are selected for the review.

XII.2 Thorium minerals

XII.2.1 Common thorium minerals

The two Gmelin volumes on minerals [1990DIT/BAR], [1991BAR/DAH] provide a good review of thorium minerals.

In the earth's crust, thorium is about three times as abundant as uranium. In minerals, thorium is frequently associated with other quadrivalent species (Zr, Hf, Ce, and U), but also with tervalent lanthanides. Table XII-1 gives a list of common thorium

containing minerals, extracted from the Mineralogical Database website[1]. In nature, ThO_2 is found mostly as solid solutions with UO_2. Conventionally, the name thorianite is used when the molar content of ThO_2 is above 75%; uranothorianite is used for such solid solutions containing $25-75\%$ ThO_2; thorian uraninite is employed when the ThO_2 content is $15-25\%$; uraninite is used when the UO_2 content is above 85%.

Table XII-1: Common thorium minerals

Mineral name	Generic chemical formula	Th content (wt%) in a typical sample
Althupite	$ThAl(UO_2)_7(PO_4)_4(OH)_5 \cdot 15(H_2O)$	8.04
Arapovite	$(U,Th)(Ca,Na)_2(K1\text{-}x[]x)Si_8O_{20}$, x~0.5	7.07
Brabantite	$CaTh(PO_4)_2$	50.22
Britholite-(Ce)	$(Ce,Ca,Th,La,Nd)_5(SiO_4,PO_4)_3(OH,F)$	18.25
Brockite	$(Ca,Th,Ce)(PO_4) \cdot (H_2O)$	31.55
Calciobetafite	$Ca_2(Ti,Nb)_2(O,OH)_7$	5.88
Cerianite-(Ce)	$(Ce,Th)O_2$	29.73
Cervandonite-(Ce)	$(Ce,Nd,La)(Fe^{+3},Fe^{+2},Ti^{+4},Al)_3SiAs(Si,As)O_{13}$	3.66
Cheralite-(Ce)	$(Ce,Ca,Th)(P,Si)O_4$	29.02
Chevkinite-(Ce)	$(Ce,La,Ca,Th)_4(Fe^{+2},Mg)_2(Ti,Fe^{+3})_3Si_4O_{22}$	1.93
Ciprianiite	$Ca_4[(Th,U,Ln)_2(Al,Va)_2[Si_4B_4O_{22}](OH,F)_2$	14.26
Coutinhoite	$Th_xBa_{1\text{-}2x}(H_2O)_y(UO_2)_2Si_5O_{13} \cdot H_2O$	3.29
Dissakisite-(La)	$(Ca,Fe,Th)(REE,Ca)(Al,Cr,Ti)_2(Mg,Fe,Al)Si_3O_{12}(OH,F)$ with La>Ce	3.98
Ekanite	$ThCa_2Si_8O_{20}$	27.08
Eylettersite	$(Th,Pb)_{(1\text{-}x)} Al_3(PO_4,SiO_4)_2(OH)_6(?)$	19.29
Fersmite	$(Ca,Ce,Na)(Nb,Ta,Ti)_2(O,OH,F)$	2.97
Grayite	$(Th,Pb,Ca)PO_4 \cdot (H_2O)$	43.73
Huttonite	$ThSiO_4$	71.59
IMA2004-001	$[(REE^+Y),U,Th,Ca,Fe](Nb,Ta,Ti)O_4$	6.83
Ilimaussite-(Ce)	$(Ba,Na)_{10}K_3Na_4.5Ce_5(Nb,Ti)_6[Si_{12}O_{36}][Si_9O_{18}(O,OH)_{24}]O_6$	1.04
Iraqite-(La)	$K(La,Ce,Th)_2(Ca,Na)_4(Si,Al)_{16}O_{40}$	9.94
Karnasurtite-(Ce)	$(Ce,La,Th)(Ti,Nb)(Al,Fe^{+3})(Si,P)_2O_7(OH)_4 \cdot 3(H_2O)(?)$	6.18
Kivuite	$(Th,Ca,Pb)H_2(UO_2)_4(PO_4)_2(OH)_8 \cdot 7(H_2O)$	8.16
Kuannersuite-(Ce)	$Ba_6Na_2REE_2(PO_4)_6FCl$	0.27
Kukharenkoite-(La)	$Ba_2(La,Th,Ce)(CO_3)_3F$	10.87
Melanocerite-(Ce)	$(Ce,Th,Ca)_5(Si,B)_3O_{12}(OH,F) \cdot n(H_2O)(?)$	5.14
Monazite-(Ce)	$(Ce,La,Nd,Th)PO_4$	4.83
Monazite-(La)	$(La,Ce,Nd)PO_4$	4.84
Monazite-(Nd)	$(Nd,Ce,La)(P,Si)O_4$	4.82
Monazite-(Sm)	$SmPO_4$	15.73

(Continued on next page)

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[1] Current web address (September 2007): www.webmineral.com

Table XII-1: (continued)

Mineral name	Generic chemical formula	Th content (wt%) in a typical sample
Mottanaite-(Ce)	$Ca_4(Ce,Ca)_2AlBe_2[Si_4B_4O_{22}]O_2$	2.30
Okanoganite-(Y)	$(Na,Ca)_3(Y,Ce)_{12}Si_6B_2O_{27}F_{14}$	1.66
Orthochevkinite	$(Ce,La,Ca,Na,Th)_4(Fe^{+2},Mg)_2(Ti,Fe^{+3})_3Si_4\,O_{22}$	7.93
Perrierite-(Ce)	$(Ce,La,Ca)_4(Fe^{+2},Mg)_2(Ti,Fe^{+3})_3Si_4O_{22}$	0.97
Polyakovite-(Ce)	$(Ce,La,Nd,Pr,Ca)_4(Mg,Fe^{++})(Cr,Fe^{+++})_2(Ti,Nb)_2Si_4O_{22}$	1.85
Polycrase-(Y)	$(Y,Ca,Ce,U,Th)(Ti,Nb,Ta)_2O_6$	6.22
Saryarkite-(Y)	$Ca(Y,Th)Al_5(SiO_4)_2(PO_4,SO_4)_2(OH)_7 \cdot 6(H_2O)$	7.53
Steacyite	$K_{1-x}(Ca,Na)_2ThSi_8O_{20}(x=0.2\ to\ 0.4)$	25.29
Steenstrupine-(Ce)	$Na_{14}Ce_6Mn^{+2}Mn^{+3}Fe^{2+}_2(Zr,Th)(Si_6O_{18})_2(PO_4)_7 \cdot 3(H_2O)$	1.85
Thorbastnasite	$Th(Ca,Ce)(CO_3)_2F_2 \cdot 3(H_2O)$	45.57
Thorianite	ThO_2	87.88
Thorite	$ThSiO_4$	71.59
Thornasite	$Na_{12}Th_3[Si_8O_{19}]_4 \cdot 18(H_2O)$	20.41
Thorogummite	$Th(SiO_4)_{1-x}(OH)_{4x}$	72.13
Thorosteenstrupine	$(Ca,Th,Mn)_3Si_4O_{11}F \cdot 6(H_2O)$	29.29
Thorutite	$(Th,U,Ca)Ti_2(O,OH)_6$	23.75
Tritomite-(Ce)	$(Ce,La,Ca,Y,Th)_5(Si,B)_3(O,OH,F)_{13}$	4.42
Tuliokite	$BaNa_6Th(CO_3)_6 \cdot 6(H_2O)$	23.79
Turkestanite	$Th(Ca,Na)_2(K_{1-x},Va_x)Si_8O_{20} \cdot n(H_2O)$	21.11
Umbozerite	$Na_3Sr_4ThSi_8(O,OH)_{24}$	18.33
Uranopolycrase	$(U,Y)(Ti,Nb,Ta)_2O_6$	5.58
Vicanite-(Ce)	$(Ca,Ce,La,Th)_{15}\,As^{+5}(As^{+3}_{0.5},Na_{0.5})Fe^{+3}Si_6BO_{40}F_7$	9.08
Yttrialite-(Y)	$(Y,Th)_2Si_2O_7$	27.79
Yttrocrasite-(Y)	$(Y,Th,Ca,U)(Ti,Fe^{+3})_2(O,OH)_6$	7.79
Zirconolite-3O	$(Ca,Fe,Y,Th)Fe(Ti,Nb)_3Zr_2O_7$	3.61
Zirkelite	$(Ca,Th,Ce)Zr(Ti,Nb)_2O_7$	6.06

In addition, it should be noted that, although the generic formula of some minerals listed in Table XII-1 does not mention thorium, this element is often present in such minerals by substitution for quadrivalent or tervalent species, in percentages that may be in excess of 10%. This is, for instance, the case for Sm-monazites. Of course, in such substitutions charge balance must be maintained and the replacement of a tervalent ion by thorium must be accompanied by an equivalent increased amount of a lower-valent cation (often Ca^{2+}) in the structure.

The thorium content given in the third column of the list is that found for a typical sample.

XII.2.2 Specific minerals

XII.2.2.1 Thorite and huttonite, ThSiO$_4$(cr)

Section XI.2.2 includes a discussion of some thermodynamic properties of thorite, including a discussion of the thorite-huttonite phase transformation.

XII.2.2.2 Thorium brannerite, ThTi$_2$O$_6$(cr)

Thorium frequently substitutes for uranium in the mineral brannerite of generic formula (U, Ca, Ce)(Ti, Fe)$_2$O$_6$. Hence ThTi$_2$O$_6$(cr) is sometimes referred to as Th-brannerite. Its enthalpy of formation has been measured [2003HEL/NAV] (see Appendix A) by high temperature drop calorimetry at 976 K, using a sodium molybdate solvent with the composition 3Na$_2$O·4MoO$_3$. Drop solution enthalpic effects were measured by dropping pellets (about 5 mg) of the powdered samples from room temperature into the solvent at the calorimeter temperature. Solution enthalpies were measured after equilibration of sample pellets above the solvent at the calorimeter temperature. In this way, the heat content increments could be taken in account.

The Th-brannerite samples were prepared by sintering ball-mill mixed stoichiometric amounts of ThO$_2$(cr) and TiO$_2$(anatase) in air at 1773 K for more than 100 hours. X-ray powder diffraction of the compounds showed them to be monoclinic, space group $C2/m$. with a = (9.8046 ± 0.0008) Å, b = (3.8187 ± 0.0003) Å, c = (7.0229 ± 0.0005) Å, and β = (118.852 ± 0.005)°, with as expected, a slightly larger cell volume than that obtained for the corresponding uranium compound. Quantitative analyses by the Rietveld method indicated a sample composition of (0.991 ± 0.003) weight fraction ThTi$_2$O$_6$ and (0.009 ± 0.001) weight fraction ThO$_2$. These results were confirmed by back-scattered electron diffraction and electron microprobe analysis with wavelength dispersion spectroscopy. After correction for the small thorium dioxide impurity, a value of (19.4 ± 1.6) kJ·mol^{-1} was reported for Reaction (XII.11) corresponding to the enthalpy of the formation reaction of thorium brannerite from the binary oxides,

$$\text{ThO}_2(\text{cr, 298.15 K}) + 2\text{TiO}_2(\text{rutile, 298.15 K}) \rightarrow \text{ThTi}_2\text{O}_6(\text{cr, 298.15 K}) \qquad \text{(XII.11)}$$

Taking their value, (19.4 ± 2.0) kJ·mol^{-1}, where the uncertainty has been recalculated by the review from individual uncertainties reported by [2003HEL/NAV], and making use of the values selected in this review for $\Delta_f H_m^\circ$ (ThO$_2$, cr, 298.15 K) = − (1226.4 ± 3.5) kJ·mol^{-1} and $\Delta_f H_m^\circ$ (TiO$_2$, rutile, 298.15 K) = − (944.0 ± 0.8) kJ·mol^{-1} we calculate:

$$\Delta_f H_m^\circ \text{ (ThTi}_2\text{O}_6\text{, cr, 298.15 K)} = -(3095.0 \pm 4.3) \text{ kJ·mol}^{-1}$$

which is the selected value.

This result indicates that Th-brannerite is entropy-stabilised and may be stable at high temperature only.
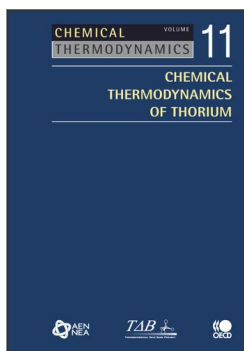
XII.2.3   General references for minerals

The following reference list concerns papers dealing with minerals of thorium, although few contain thermodynamic data. These references should be useful for readers interested in thorium minerals. They will also provide a source from which a more comprehensive list of minerals could be generated. Since this is a specialised area, these references are included hereunder rather than in the general bibliography.

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