

APPENDICES OF

Solubility study of Ti,Zr-based ceramics designed to immobilise long-lived radionuclides

Gilles Leturcq, Thierry Advocat, Kaye Hart, Gilles Berger, Jacques Lacombe and Armand Bonnetier

Appendix 1: Thermodynamic data from literature ñ solid species

Chemical species	G_f° (kJ/mol)	H_f° (kJ/mol)	S_f° (J/mol K)	C_p (J/mol K)	Reference
Al ₂ O ₃	-1582.26	-1675.70	50.92	79.03	Cox et al. (1989)
Al(OH) ₃	-1156.40	-1294.63	68.44	91.76	Phillips et al. (1988)
Al ₂ TiO ₅	-2489.23	-2635.5	109.6	136.40	Babushkin et al. (1985)
BaO	-525.35	-553.54	70.42	47.28	Barin (1989)
BaAl ₂ O ₄	-2212.37	-2325.89	148.53	125.07	Barin (1989)
BaSiO ₃	-1540.31	-1623.60	109.6	90.00	Barin (1989)
Ba ₂ SiO ₄	-2175.14	-2287.80	176.1	134.89	Barin (1989)
Ba ₂ SiO ₄	-2410.97	-2548.06	153.13	134.21	Barin (1989)
BaSi ₂ O ₅	-3963.07	-4184.80	258.20	224.60	Barin (1989)
Ba ₂ Si ₃ O ₈	-1572.44	-1659.80	107.90	102.47	Barin (1989)
BaTiO ₃	-2132.90	-2243.00	196.60	152.63	Barin (1989)
Ba ₂ TiO ₄	-1694.68	-1779.46	124.68	100.71	Barin (1989)
BaZrO ₃	-603.51	-635.09	38.07	42.12	Barin (1989)
CaO	-2208.82	-2326.30	114.22	120.79	Barin (1989)
CaAl ₂ O ₄	-2801.42	-2958	127.09	164.35	Barin (1989)
Ca ₂ Al ₂ O ₅	-3411.79	-3587.80	205.90	209.70	Barin (1989)
Ca ₃ Al ₂ O ₆	-1549.66	-1634.94	81.92	85.27	Barin (1989)
CaSiO ₃ (wollastonite)	-2198.59	-2315.22	120.79	126.65	Barin (1989)
Ca ₂ SiO ₄ (olivine)	-2783.90	-2929.20	168.60	171.88	Barin (1989)
Ca ₂ SiO ₄ (olivine)	-3122.04	-3298.20	141.40	165.7	Barin (1989)
Ca ₃ SiO ₅	-4002.22	-4227.90	199.28	211.31	Barin (1989)
CaAl ₂ SiO ₆ (pyroxene)	-3782.86	-3981.50	210.00	205.43	Barin (1989)
CaAl ₂ Si ₂ O ₈ (anorthite)	-6280.41	-6646.16	241.42	323.14	Barin (1989)
Ca2Al2SiO7	-1575.2	-1660.6	93.64	97.65	Wagman et al.(1982)

Ca ₃ Al ₂ Si ₃ O ₁₂	-3751.01	-3950.50	234.70	239.32	Barin (1989)
CaTiO ₃ (perovskite)	-5386.85	-5671.66	328.44	337.81	Barin (1989)
Ca ₃ Ti ₂ O ₇	-2461.78	-2603.30	129.20	138.95	Barin (1989)
Ca ₄ Ti ₃ O ₁₀	-1681.06	-1766.90	100.08	96.57	Barin (1989)
CaTiSiO ₅ (titanite)	-3514.6	-3713.8	193.3	211.9	Putnam et al. (1999)
CaZrO ₃	-856.44	-910.86	41.46	44.59	Barin (1989)
CaZrTi ₂ O ₇ (zirconolite)	-889.41	-944.75	50.29	55.10	Barin (1989)
SiO ₂	-883.00	-938.72	49.91	55.27	Phillips et al. (1988)
TiO ₂ (rutile)	-1547.97	-1720.5	129.7	56.19	Babushkin et al. (1985)
TiO ₂ (anatase)	-1039.72	-1097.46	50.36	98.74	Chase et al. (1985)
Zr(OH) ₄ (c)	-1909.33	-2023.80	84.03		Barin (1989)
ZrO ₂ (zirconia)					
ZrSiO ₄ (zircon)					

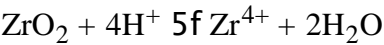
Appendix 2: Thermodynamic data - aqueous species

Chemical species	G_f° (kJ/mol)	H_f° (kJ/mol)	Reference
			Cox et al. (1989)
H ₂ O	-237.14		Phillips et al. (1988)
OH ⁻	-157.20	-285.83	Castet et al. (1993)
Al ³⁺	-488.7	-230.03	Castet et al. (1993)
Al(OH) ²⁺	-696.3	-537.2	Castet et al. (1993)
Al(OH) ₂ ⁺	-903.7	-769.0	Castet et al. (1993)
Al(OH) ₃ aq	-1109.2	-1014.2	Castet et al. (1993)
Al(OH) ₄ ⁻	-1305.6	-1251.8	Phillips et al. (1988)
Ca ²⁺	-552.90	-1495.8	Phillips et al. (1988)
Ti ⁴⁺	-391.60	-543.1	Phillips et al.
	-861.47	-449.80	
		-976.20	
2+	-		

Ti(OH) ₂	1084.92	(1988)
Ti(OH) ₃ ⁺	-1229.40	Phillips et al.
	1308.37	(1988)
Ti(OH) _{4aq}	-1735.60	Phillips et al.
	-	(1988)
Ti(OH) ₅ ⁻	1531.32	Phillips et al.
	-933.50	(1988)
ZrO ²⁺	-840.62	Phillips et al.

Latimer (1952)

Reaction	log <i>K</i> _{25fbC}	Reference
Zr ⁴⁺ + H ₂ O 5f Zr(OH) ³⁺ + H ⁺		
Zr ⁴⁺ + 2H ₂ O 5f Zr(OH) ₂ ²⁺ + 2H ⁺	0.3	
Zr ⁴⁺ + 3H ₂ O 5f Zr(OH) ₃ ⁺ + 3H ⁺	-1.7 -5.1	Allard et al. (1980) ;
Zr ⁴⁺ + 4H ₂ O 5f Zr(OH) _{4aq} + 4H ⁺	-9.7 -16.0	Baes and Mesmer (1986)
Zr ⁴⁺ + 5H ₂ O 5f Zr(OH) ₅ ⁻ + 5H ⁺	-1.9	



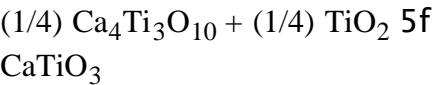
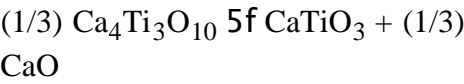
Chemical species	<i>G</i> _f [°] (kJ/mol)	<i>H</i> _f [°] (kJ/mol)	Reference
Zr ⁴⁺	-554.83		
	-793.64	-610.71	
Zr(OH) ³⁺	-	-880.45	
	1019.34		
Zr(OH) ₂ ²⁺	-	-1135.36	
	-		
Zr(OH) ₃ ⁺	1237.04	-1381.24	this study
	-	-1619.40	
Zr(OH) _{4aq}	1447.89		
	-	-1846.59	
Zr(OH) ₅ ⁻	-		
	1649.05		

Appendix 3: Chemical reactions for the formation of perovskite from oxide reactants and associated free energy and enthalpy of formation.

44*G*_f - 44*H* - 44*H*

Chemical reaction	$44G_r$ kJ/mol	f_r kJ/mol
$\text{CaO} + \text{TiO}_2 \rightarrow 5f \text{ CaTiO}_3$		
$\text{CaAl}_2\text{O}_4 + \text{TiO}_2 \rightarrow 5f \text{ CaTiO}_3 + \text{Al}_2\text{O}_3$		
$\text{CaTiSiO}_5 \rightarrow 5f \text{ CaTiO}_3 + \text{SiO}_2$		
$\text{BaTiO}_3 + \text{CaO} \rightarrow 5f \text{ CaTiO}_3 + \text{BaO}$		
$\text{CaZrO}_3 + \text{TiO}_2 \rightarrow 5f \text{ CaTiO}_3 + \text{ZrO}_2$		
$\text{CaTiSiO}_5 + \text{ZrO}_2 \rightarrow 5f \text{ CaTiO}_3 + \text{ZrSiO}_4$	-1492.92 -1515.97	-1579.84 -1595.35
$\text{CaSiO}_3 + \text{CaZrO}_3 + \text{TiO}_2 \rightarrow 5f \text{ CaTiO}_3 + \text{ZrSiO}_4 + \text{CaO}$	-1605.34 -1650.60	-1692.45 -1741.34
$\text{CaSiO}_3 + \text{TiO}_2 \rightarrow 5f \text{ CaTiO}_3 + \text{SiO}_2$	-1530.74	-1614.19
$\text{CaSiO}_3 + \text{BaZrO}_3 + \text{TiO}_2 \rightarrow 5f \text{ CaTiO}_3 + \text{ZrSiO}_4 + \text{BaO}$	-1592.18 -1607.29	-1676.96 -1687.7
$\text{CaZrTi}_2\text{O}_7 \rightarrow 5f \text{ CaTiO}_3 + \text{ZrO}_2 + \text{TiO}_2$	-1582.62	-1668.83
$2 \text{ CaTiSiO}_5 \rightarrow 5f \text{ CaTiO}_3 + \text{CaSiO}_3 + \text{SiO}_2 + \text{TiO}_2$	-1699.08 -1585.47	-1781.80 -1671.59
$\text{BaTiO}_3 + \text{CaSiO}_3 \rightarrow 5f \text{ CaTiO}_3 + \text{BaSiO}_3$	-1628.05	-1716.06
$\text{BaTiO}_3 + \text{CaZrO}_3 \rightarrow 5f \text{ CaTiO}_3 + \text{BaZrO}_3$	-1581.79 -1558.81	-1671.14 -1647.25
$\text{CaSiO}_3 + \text{CaZrTi}_2\text{O}_7 \rightarrow 5f 2 \text{ CaTiO}_3 + \text{ZrSiO}_4$	-1577.46 -1335.23	-1662.47 -1418.33
$\text{BaO} + \text{CaO} + 2 \text{ TiO}_2 \rightarrow 5f \text{ CaTiO}_3 + \text{BaTiO}_3$	-1547.65 -1546.80	-1637.24 -1631.75
$\text{CaO} + \text{CaZrTi}_2\text{O}_7 \rightarrow 5f \text{ CaTiO}_3 + \text{CaZrO}_3 + \text{TiO}_2$	-1573.75 -1594.45	-1657.71 -1678.86
$(1/3) \text{ Ca}_3\text{Ti}_2\text{O}_7 + (1/3) \text{ TiO}_2 \rightarrow 5f \text{ CaTiO}_3$	-1569.07	-1654.10
$(1/2) \text{ Ca}_3\text{Ti}_2\text{O}_7 \rightarrow 5f \text{ CaTiO}_3 + (1/2)$		

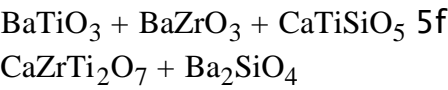
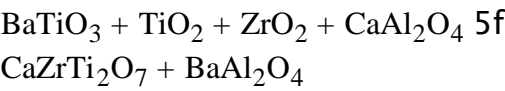
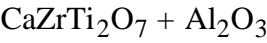
CaO



AVERAGE **-1569** **-1654**

Appendix 3: Chemical reactions for the formation of zirconolite from oxide reactants and associated free energy and enthalpy of formation.

Chemical reaction	$44G_f - 44G_r$ kJ/mol	$44H_f - 44H_r$ kJ/mol
CaTiO ₃ + ZrO ₂ + TiO ₂ 5f CaZrTi ₂ O ₇		
2 TiO ₂ + CaO + ZrO ₂ 5f CaZrTi ₂ O ₇		
TiO ₂ + CaTiSiO ₅ + ZrO ₂ 5f CaZrTi ₂ O ₇ + SiO ₂		
TiO ₂ + CaTiO ₃ + ZrSiO ₄ 5f CaZrTi ₂ O ₇ + SiO ₂	-3504.38	-3702.81
TiO ₂ + CaTiSiO ₅ + ZrSiO ₄ 5f CaZrTi ₂ O ₇ + 2 SiO ₂	-3422.05 -3534.47	-3622.05 -3734.66
2 TiO ₂ + CaSiO ₃ + ZrO ₂ 5f CaZrTi ₂ O ₇ + SiO ₂	-3517.53 -3547.62	-3718.29 -3750.14
BaZrO ₃ + 2 TiO ₂ + CaO 5f CaZrTi ₂ O ₇ + BaO	-3511.75	-3711.04
BaTiO ₃ + CaZrO ₃ + TiO ₂ 5f CaZrTi ₂ O ₇ + BaO	-3551.66 -3617.56	-3750.50 -3817.90
CaZrO ₃ + 2 TiO ₂ 5f CaZrTi ₂ O ₇	-3459.87	-3656.40
CaZrO ₃ + CaTiO ₃ + TiO ₂ 5f CaZrTi ₂ O ₇ + CaO	-3542.2 -3527.1	-3737.16 -3726.42
CaTiO ₃ + CaTiSiO ₅ + ZrO ₂ 5f CaZrTi ₂ O ₇ + CaSiO ₃	-3510.16 -3445.10	-3710.05 -3637.56
2 CaTiO ₃ + ZrSiO ₄ 5f CaZrTi ₂ O ₇ + CaSiO ₃	-3498.02 -3553.76	-3702.43 -3754.76
CaAl ₂ O ₄ + 2 TiO ₂ + ZrO ₂ 5f		



AVERAGE **-3516** **-3715**

Appendix 4: Chemical reactions for the formation of titanite from oxide reactants and associated free energy and enthalpy of formation.

Chemical reaction	$44G_f - 44G_r$ kJ/mol	$44H_f - 44H_r$ kJ/mol
$\text{CaSiO}_3 + \text{TiO}_2$ 5f CaTiSiO_5		
$\text{CaTiO}_3 + \text{SiO}_2$ 5f CaTiSiO_5		
$\text{Ca}_2\text{SiO}_4 + \text{TiO}_2$ 5f $\text{CaTiSiO}_5 + \text{CaO}$		
$(1/3) \text{Ca}_3\text{Al}_2\text{Si}_3\text{O}_{12} + \text{TiO}_2$ 5f $\text{CaTiSiO}_5 + (1/3) \text{Al}_2\text{O}_3$	-2439.06	-2579.69
$\text{Ca}_3\text{SiO}_5 + \text{TiO}_2$ 5f $\text{CaTiSiO}_5 + 2 \text{CaO}$	-2431.69	-2571.45
$\text{Ca}_4\text{Ti}_3\text{O}_{10} + \text{SiO}_2$ 5f $\text{CaTiSiO}_5 + 2 \text{CaTiO}_3 + \text{CaO}$	-2484.49	-2624.87
$(1/2) \text{Ca}_3\text{Ti}_2\text{O}_7 + \text{SiO}_2$ 5f $\text{CaTiSiO}_5 + (1/2) \text{CaO}$	-2455.46	-3601.57
$\text{CaZrTi}_2\text{O}_7 + \text{CaSiO}_3$ 5f $\text{CaTiSiO}_5 + \text{CaZrO}_3 + \text{TiO}_2$	-2466.29 -2489.30	-2603.77 -2626.24
$\text{CaAl}_2\text{SiO}_6 + \text{TiO}_2$ 5f $\text{CaTiSiO}_5 + \text{Al}_2\text{O}_3$	-2430.19	-2568.56
$(1/2) \text{CaAl}_2\text{Si}_2\text{O}_8 + \text{CaTiO}_3$ 5f $\text{CaTiSiO}_5 + (1/2) \text{CaAl}_2\text{O}_4$	--2493.79 -2429.19	-2637.09 -2567.25
$\text{CaZrTi}_2\text{O}_7 + \text{Ca}_2\text{SiO}_4$ 5f $\text{CaTiSiO}_5 + \text{CaZrO}_3 + \text{CaTiO}_3$	-2471.95 -2456.89	-2611.39 -2601.52
$(1/2) \text{CaZrTi}_2\text{O}_7 + \text{CaSiO}_3$ 5f $\text{CaTiSiO}_5 + (1/2) \text{CaZrO}_3$	-2466.43 -2441.91	-2608.39 -2582.45
$\text{CaZrTi}_2\text{O}_7 + \text{SiO}_2$ 5f $\text{CaTiSiO}_5 + \text{TiO}_2 + \text{ZrO}_2$	-2349.36	-2490.69
$\text{CaO} + \text{TiO}_2 + \text{SiO}_2$ 5f CaTiSiO_5	-2402.16	-2544.11
$\text{Ca}_2\text{SiO}_4 + 2 \text{TiO}_2$ 5f $\text{CaTiSiO}_5 + \text{CaTiO}_3$	-2425.51	-2564.96

(1/4) $\text{Ca}_4\text{Ti}_3\text{O}_{10} + (1/4) \text{TiO}_2 + \text{SiO}_2$ 5f CaTiSiO_5	-2455.38	-2593.35
(1/2) [$\text{Ca}_4\text{Ti}_3\text{O}_{10} + \text{ZrO}_2 + \text{TiO}_2$] + SiO_2 5f $\text{CaTiSiO}_5 + (1/2) [\text{CaO} + \text{CaZrTi}_2\text{O}_7]$	-2406.96 -2450.89	-2545.48 -2589.72
$\text{Ca}_4\text{Ti}_3\text{O}_{10} + \text{SiO}_2 + \text{TiO}_2$ 5f $\text{CaTiSiO}_5 + 3 \text{CaTiO}_3$	-2569.03	-2707.65
(1/3) $\text{Ca}_4\text{Ti}_3\text{O}_{10} + \text{SiO}_2$ 5f $\text{CaTiSiO}_5 + (1/3) \text{CaO}$	-2550.66	-2698.31
(1/3) $\text{Ca}_4\text{Ti}_3\text{O}_{10} + (2/3) \text{CaO} + \text{Ca}_2\text{Al}_2\text{SiO}_7$ 5f $\text{CaTiSiO}_5 + \text{Ca}_3\text{Al}_2\text{O}_6$	-2531.45	-2680.05
(1/3) [$\text{Ca}_4\text{Ti}_3\text{O}_{10} + \text{Ca}_3\text{Al}_2\text{Si}_3\text{O}_{12}$] 5f $\text{CaTiSiO}_5 + (1/3) [\text{CaO} + \text{Ca}_3\text{Al}_2\text{O}_6]$		
(1/3) $\text{Ca}_3\text{Al}_2\text{Si}_3\text{O}_{12} + \text{CaTiO}_3$ 5f $\text{CaTiSiO}_5 + (1/3) \text{Ca}_3\text{Al}_2\text{O}_6$		
AVERAGE	-2459	-2600

Appendix 5: Chemical reactions of formation of Ca_2SiO_4 from oxide reactants and associated free energy and enthalpy of formation.

Chemical reaction	$44G_f - 44G_r$ kJ/mol	$44H_f - 44H_r$ kJ/mol
$\text{CaO} + \text{CaSiO}_3$ 5f Ca_2SiO_4		
Ca_3SiO_5 5f $\text{Ca}_2\text{SiO}_4 + \text{CaO}$	-2153.17	-2270.03
2CaSiO_3 5f $\text{Ca}_2\text{SiO}_4 + \text{SiO}_2$	-2180.39	-2294.11
$\text{CaAl}_2\text{SiO}_6 + \text{CaO}$ 5f $\text{Ca}_2\text{SiO}_4 + \text{Al}_2\text{O}_3$	-2242.87	-2359.02
$\text{Ca}_3\text{Al}_2\text{Si}_3\text{O}_{12}$ 5f $\text{Ca}_2\text{SiO}_4 + \text{CaAl}_2\text{Si}_2\text{O}_8$	-2143.30	-2257.59
$2 \text{CaAl}_2\text{Si}_2\text{O}_8$ 5f $\text{Ca}_2\text{SiO}_4 + 2 \text{Al}_2\text{SiO}_5 + \text{SiO}_2$	-2278.18 -2262.22	-2418.26 -2364.31
2CaSiTiO_5 5f $\text{Ca}_2\text{SiO}_4 + \text{SiO}_2 + 2 \text{TiO}_2$	-2288.30	-2406.25
$2\text{CaTiO}_3 + \text{Ba}_2\text{SiO}_4$ 5f $\text{Ca}_2\text{SiO}_4 + 2 \text{BaTiO}_3$	-2180.76 -2147.89	-2289.40 -2262.70
$2 \text{CaZrO}_3 + \text{Ba}_2\text{SiO}_4$ 5f $\text{Ca}_2\text{SiO}_4 + 2 \text{BaZrO}_3$	-2109.57	-2212.07
$2 \text{CaAl}_2\text{O}_4 + \text{SiO}_2$ 5f $\text{Ca}_2\text{SiO}_4 + 2 \text{Al}_2\text{O}_3$		
AVERAGE	-2199	-2313

Appendix 6: Chemical reactions for the formation of pyroxene from oxide reactants and associated free energy and enthalpy of formation.

Chemical reaction	$44G_f - 44G_r$ kJ/mol	$44H_f - 44H_r$ kJ/mol
$\text{CaO} + \text{Al}_2\text{O}_3 + \text{SiO}_2 \rightarrow \text{CaAl}_2\text{SiO}_6$		
$\text{CaSiO}_3 + \text{Al}_2\text{O}_3 \rightarrow \text{CaAl}_2\text{SiO}_6$		
$\text{CaAl}_2\text{Si}_2\text{O}_8 \rightarrow \text{CaAl}_2\text{SiO}_6 + \text{SiO}_2$	-3042.21	-3221.65
$\text{Ca}_2\text{SiO}_4 + \text{Al}_2\text{O}_3 \rightarrow \text{CaAl}_2\text{SiO}_6 + \text{CaO}$	-3131.91 -3145.78	-3310.64 -3317.04
$\text{CaAl}_2\text{O}_4 + \text{SiO}_2 \rightarrow \text{CaAl}_2\text{SiO}_6$	-3177.34	-3355.83
$\text{CaO} + \text{Al}_2\text{SiO}_5 \rightarrow \text{CaAl}_2\text{SiO}_6$	-3065.26	-3237.16
$\text{Ca}_3\text{Al}_2\text{Si}_3\text{O}_{12} \rightarrow \text{CaAl}_2\text{SiO}_6 + 2 \text{CaSiO}_3$	-3046.40 -3181.10	-3225.40 -3376.28
$\text{Ca}_2\text{Al}_2\text{SiO}_7 \rightarrow \text{CaAl}_2\text{SiO}_6 + \text{CaO}$	-3179.35	-3346.41
$\text{CaTiSiO}_5 + \text{Al}_2\text{O}_3 \rightarrow \text{CaAl}_2\text{SiO}_6 + \text{TiO}_2$	-3154.63 -3061.21	-3334.26 -3228.48
$\text{Ca}_3\text{Al}_2\text{O}_6 + \text{SiO}_2 \rightarrow \text{CaAl}_2\text{SiO}_6 + 2 \text{CaO}$	-3159.14	-3334.72
$\text{Ca}_3\text{SiO}_5 + \text{Al}_2\text{O}_3 \rightarrow \text{CaAl}_2\text{SiO}_6 + 2 \text{CaO}$		
AVERAGE	-3122	-3299

Appendix 8: Comparison between approximations and real values of 44Gf and 44Hf of perovskite, zirconolite, titanite, olivine and pyroxene, and relative errors. Ca_2SiO_4

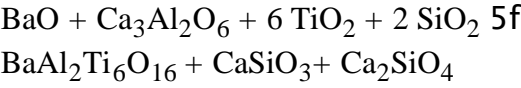
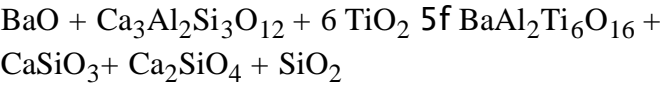
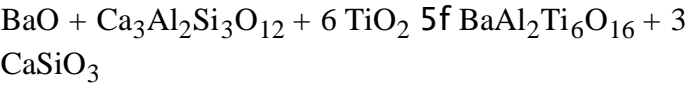
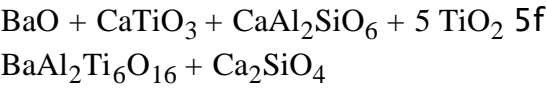
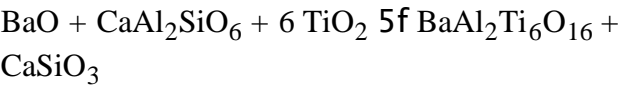
	$44G_f$ est.	$44G_f$ p.r.	$44G_f$ est. - $44G_f$ p.r.	% error
$\text{CaZrTi}_2\text{O}_7$	-3516.21	-3514.60	-1.61	0.046
CaTiO_3	-1575.24	-1575.20	-0.04	0.003
Ca_2SiO_4	-2198.66	-2198.80	0.14	-0.006
$\text{CaAl}_2\text{SiO}_6$	-3122.21	-3122.00	-0.21	0.007
CaTiSiO_5	-2459.00	-2461.80	2.80	-0.114
	$44H_f$ est.	$44H_f$ p.r.	$44H_f$ est. - $44H_f$ p.r.	% error
$\text{CaZrTi}_2\text{O}_7$	-3715.48	-3713.80	-1.68	0.045

CaTiO ₃	-1660.87	-1660.60	-0.27	0.016
-2313.37	-2315.20	1.83	-0.079	CaAl ₂ SiO ₆
-3298.90		-3298.20		-0.70

44Gf est. and 44Hf est are the estimated values of 44Gf and 44Hf , 44Gf p.r. and 44Gf p.r. are the previous reported values in Appendices 3-7. Appendix 9: Chemical reactions for the formation of hollandite from oxide reactants and associated free energy and enthalpy of formation.

Chemical reaction	$\frac{44G_f - 44G_r}{\text{kJ/mol}}$	$\frac{44H_f - 44H_r}{\text{kJ/mol}}$
BaO + Al ₂ O ₃ + 6 TiO ₂ rut 5f BaAl ₂ Ti ₆ O ₁₆		
BaAl ₂ O ₄ + 6 TiO ₂ rut 5f BaAl ₂ Ti ₆ O ₁₆		
Al ₂ O ₃ + 5 TiO ₂ rut + BaTiO ₃ 5f BaAl ₂ Ti ₆ O ₁₆		
CaAl ₂ O ₄ + 5 TiO ₂ rut + BaTiO ₃ 5f BaAl ₂ Ti ₆ O ₁₆ + CaO		
BaO + Al ₂ O ₃ + 6 CaTiO ₃ 5f BaAl ₂ Ti ₆ O ₁₆ + 6 CaO		
BaAl ₂ O ₄ + 6 CaTiO ₃ 5f BaAl ₂ Ti ₆ O ₁₆ + 6 CaO		
BaSiO ₃ + Al ₂ O ₃ + 6 TiO ₂ rut 5f BaAl ₂ Ti ₆ O ₁₆ + SiO ₂		
BaSiO ₃ + Al ₂ O ₃ + 6 CaTiO ₃ 5f BaAl ₂ Ti ₆ O ₁₆ + 5 CaO + CaSiO ₃		
Al ₂ O ₃ + 5 CaTiO ₃ + BaTiO ₃ 5f BaAl ₂ Ti ₆ O ₁₆ + 5 CaO		
BaO + Al ₂ O ₃ + 6 CaTiSiO ₅ 5f BaAl ₂ Ti ₆ O ₁₆ + 6 CaSiO ₃	-7444.04	-7897.73
	-7548.81	-7994.37
BaAl ₂ O ₄ + 6 CaTiSiO ₅ 5f BaAl ₂ Ti ₆ O ₁₆ + 6 CaSiO ₃	-7601.73	-8059.23
	-7624.78	-8074.75
Al ₂ O ₃ + 5 CaTiSiO ₅ + BaTiO ₃ 5f BaAl ₂ Ti ₆ O ₁₆ + 5 CaSiO ₃	-7938.03	-8382.29
	-8042.80	-8478.93
BaZrO ₃ + + Al ₂ O ₃ + 6 TiO ₂ rut 5f BaAl ₂ Ti ₆ O ₁₆ + ZrO ₂	-7602.56	-8056.93
	-8006.85	-8452.49
BaO + Al ₂ O ₃ + 3 CaZrTi ₂ O ₇ 5f BaAl ₂ Ti ₆ O ₁₆ + 3 CaZrO ₃	-8013.39	-8463.03
	-7580.35	-8039.42
BaAl ₂ O ₄ + 3 CaZrTi ₂ O ₇ 5f BaAl ₂ Ti ₆ O ₁₆ + 3		

CaZrO ₃	-7685.12	-8136.06
CaAl ₂ SiO ₆ + 5 TiO ₂ rut + BaTiO ₃ 5f BaAl ₂ Ti ₆ O ₁₆	-7715.32	-8177.31
+ CaSiO ₃	-7573.65	-8026.17
CaAl ₂ SiO ₆ + 4 TiO ₂ rut + BaTiO ₃ + CaTiO ₃ 5f BaAl ₂ Ti ₆ O ₁₆ + Ca ₂ SiO ₄	-7608.23	-8069.93
	-7713.00	-8166.58
Ca ₂ Al ₂ SiO ₇ + 5 TiO ₂ rut + BaTiO ₃ 5f BaAl ₂ Ti ₆ O ₁₆ + Ca ₂ SiO ₄	-7591.86	-8046.79
	-7628.76	-8082.37
CaAl ₂ Si ₂ O ₈ + 5 TiO ₂ rut + BaTiO ₃ + CaTiO ₃ 5f BaAl ₂ Ti ₆ O ₁₆ + CaSiO ₃ + CaTiSiO ₅	- 7603.74	-8049.82
Ca ₃ Al ₂ O ₆ + 5 TiO ₂ rut + BaTiO ₃ 5f BaAl ₂ Ti ₆ O ₁₆ + 3 CaO	- 7585.51	-8033.79
	-7620.73	-8066.07
Ca ₃ Al ₂ O ₆ + 5 TiO ₂ rut + BaTiO ₃ + 3 SiO ₂ 5f BaAl ₂ Ti ₆ O ₁₆ + 3 CaSiO ₃	-7450.51	-7900.75
	-7373.73	-7823.79
Ca ₃ Al ₂ O ₆ + 8 TiO ₂ rut + BaTiO ₃ 5f BaAl ₂ Ti ₆ O ₁₆ + 3 CaTiO ₃	-7395.90	-7842.89
	-7650.91	-8124.87
Ca ₃ Al ₂ O ₆ + 5 TiO ₂ rut + BaTiO ₃ + 2 SiO ₂ 5f BaAl ₂ Ti ₆ O ₁₆ + CaSiO ₃ + Ca ₂ SiO ₄	-7695.19	-8168.68
	-7929.05	-8364.94
Ca ₃ Al ₂ Si ₃ O ₁₂ + 5 TiO ₂ rut + BaTiO ₃ 5f BaAl ₂ Ti ₆ O ₁₆ + 3 CaSiO ₃	-7794.78	-8239.95
Ca ₃ Al ₂ Si ₃ O ₁₂ + 5 TiO ₂ rut + BaTiO ₃ 5f BaAl ₂ Ti ₆ O ₁₆ + CaSiO ₃ + Ca ₂ SiO ₄ + SiO ₂	-7964.55	-8407.22
	-7937.71	-8381.28
3 Ca ₃ Ti ₂ O ₇ +Al ₂ O ₃ + BaO 5f BaAl ₂ Ti ₆ O ₁₆ + 9 CaO	-7617.50	-8054.78
	-7499.35	-7942.42
2Ca ₃ Ti ₂ O ₇ +BaTiO ₃ +TiO ₂ rut +CaAl ₂ Si ₂ O ₈ 5f BaAl ₂ Ti ₆ O ₁₆ + CaO + 2 Ca ₃ SiO ₅	-7434.17	-7885.29
	-7471.08	-7920.86
2 Ca ₄ Ti ₃ O ₁₀ + BaSiO ₃ + CaAl ₂ Si ₂ O ₈ 5f BaAl ₂ Ti ₆ O ₁₆ + 3 Ca ₃ SiO ₅	-7493.22	-7963.36
Ca ₄ Ti ₃ O ₁₀ + Ca ₃ Ti ₂ O ₇ + BaTiO ₃ + CaAl ₂ Si ₂ O ₈ 5f BaAl ₂ Ti ₆ O ₁₆ + 2 Ca ₃ SiO ₅ + 2 CaO	-7537.50	-8007.171
	-7238.21	-7681.38
2 Ca ₄ Ti ₃ O ₁₀ + BaAl ₂ O ₄ + 4 SiO ₂ 5f BaAl ₂ Ti ₆ O ₁₆ + 4 Ca ₂ SiO ₄		
2 Ca ₄ Ti ₃ O ₁₀ + BaAl ₂ O ₄ + 8 TiO ₂ 5f BaAl ₂ Ti ₆ O ₁₆		



AVERAGE **-7645** **-8096**

Appendix 7: Chemical reactions for the formation of Ti hydroxide from oxide reactants and associated free energy and enthalpy of formation.

Chemical reaction	$44G_f - 44G_r$ kJ/mol	$44H_f - 44H_r$ kJ/mol
TiO ₂ (anat) + 2 H ₂ O 5f Ti(OH) ₄		
TiO ₂ (rut) + 2 H ₂ O 5f Ti(OH) ₄	-1357.63	-1510.38
TiO ₂ (rut) + Zr(OH) ₄ 5f Ti(OH) ₄ + ZrO ₂	-1363.77	-1516.41
	-1397.65	-1567.78
Ti(OH) ₄ aq 5f Ti(OH) ₄	-1308.37	-1482.50
2 Ba(OH) ₂ + TiO ₂ (rut) 5f Ti(OH) ₄ + 2 BaO	-1557.71	-1730.26
	-1382.77	-1572.48
2 Al(OH) ₃ + TiO ₂ (rut) 5f Ti(OH) ₄ + Al ₂ O ₃ + H ₂ O		
AVERAGE	-1395	-1563