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Thermochemistry and the enthalpy of formation of synthetic end-member ($CaTiSiO_5$) titanite

DIMITRIOS XIROUCHAKIS,[1,2] SOPHIE FRITSCH,[1,3]* ROBERT L. PUTNAM,[1,3]
ALEXANDRA NAVROTSKY,[1,3] AND DONALD H. LINDSLEY[1,2]

[1]Center for High Pressure Research, State University of New York at Stony Brook, Stony Brook, New York 11794-2100, U.S.A.
[2]Department of Earth and Space Sciences, State University of New York at Stony Brook, Stony Brook,
New York 11794-2100, U.S.A.
[3]Department of Geosciences, Princeton University, Princeton, New Jersey 08544, U.S.A.

ABSTRACT

The enthalpy of drop solution of a quickly quenched, clear, titanite glass sample and several synthetic, polycrystalline, samples was measured in a Calvet-type calorimeter in $2PbO\cdot B_2O_3$ solvent at 702 °C. The enthalpy of formation of stoichiometric, end-member ($CaTiSiO_5$) titanite is redetermined to be -119.59 ± 2.24 kJ/mol from the oxides and -2610.13 ± 2.90 kJ/mol from the elements at 25 °C. The new value is either 8.725 or 13.525 kJ/mol more negative than the currently accepted values derived from calorimetry and phase-equilibrium experiments. The presence of impurities and possibly nonstoichiometry in the original sample, used in the previous calorimetric studies, are probably responsible for this discrepancy. This interpretation is further supported by the correlation of the variations in the measured enthalpies of drop solution to the documented physical differences among the synthetic polycrystalline samples used in this study. At 25 °C the enthalpy of formation of $CaTiSiO_5$ glass is -38.775 ± 3.37 kJ/mol from the oxides and -2529.31 ± 3.84 from the elements and the enthalpy of vitrification of titanite is 80.78 ± 3.59 kJ/mol.

INTRODUCTION

Titanite is an extremely common accessory mineral. Moreover, titanite-forming reactions can place constraints on the stability of more abundant rock-forming minerals (e.g., iron titanium oxides, pyroxene, and garnet). Such reactions are also good indicators of changes in pressure, temperature, and oxygen fugacity conditions (e.g., Wones 1989; Manning and Bohlen 1991; Xirouchakis and Lindsley 1995; in preparation). Titanite can also have industrial applications because titanite-based ceramics and glass-ceramics are possible hosts for nuclear waste (e.g., Hayward and Cechetto 1982; Hayward et al. 1990). Accurately known thermodynamic data are useful in calculations of the stability of titanite (e.g., in natural waters, crustal rocks) and in the thermodynamic modelling of experiments involving titanite where agreement between calorimetry and well-characterized, reversed experiments is sought (Berman 1988; Holland and Powell 1990; Xirouchakis and Lindsley 1995; in preparation).

The currently available thermochemical data were first derived from low-temperature heat-capacity and high-temperature heat-content measurements by King et al. (1954) and subsequently from hydrofluoric acid (HF) solution calorimetry by Todd and Kelley (1956). In both studies the same sample was used (King et al. 1954). The original study reports that a mixture of calcium carbonate, titania, and silica was heated in platinum 50 °C above the melting point, held there for an unspecified time, and then poured on a polished nickel plate. Presumably, this method was followed to ensure uniform composition in the resulting glass, provided that the mixture melted completely. However, King et al. (1954) described the product of this procedure as a crystalline mass. This suggests that either the mixture did not completely melt or if it melted then it apparently crystallized during cooling. Xirouchakis et al. (1996; 1997) have argued that titanite synthesis by slow crystallization of stoichiometric melts and by subsolidus annealing of titanite glasses may result in impure, possibly nonstoichiometric samples that have a larger unit cell probably because of vacancies in the Ca, Si, or both sites. Therefore, it is argued that the early calorimetric studies used samples that did not meet modern standards of phase purity and stoichiometry. Recently, Robie and Hemingway (1995) revised the enthalpy of formation of titanite (about +4 kJ) to agree with the optimized titanite data in the internally consistent thermodynamic data sets of Berman (1988) and Holland and Powell (1990). However, the choice of calorimetric data on which to base the thermodynamic analysis of titanite-bearing reactions can affect the optimized values for

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* Present address: Laboratoire de Chemie des Materiaux Inorganiques, Universite Paul Sabutier, 118 Route de Marbonne, 31062 Toulouse Cedex, France

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TABLE 1. Electron microprobe analyses of synthetic samples either referenced or used in this study

Sample		Glass 93	Glass 96	93-1	95-2	96-1	96-2
No. of analyses	Ideal Titanite	17	33	61	34	34	49
Element wt%							
Ca	20.44	20.02(0.21)	20.25(0.20)	20.13(0.32)	20.48(0.35)	20.47(0.48)	20.61(0.20)
Ti	24.43	23.93(0.50)	24.17(0.33)	24.95(0.63)	24.70(0.54)	24.83(0.61)	24.37(0.24)
Si	14.32	14.31(0.46)	14.47(0.20)	13.69(0.51)	14.28(0.38)	14.19(0.22)	14.58(0.13)
O	40.81	40.36(0.57)	40.76(0.90)	40.38(0.92)	40.52(1.04)	40.86(0.43)	40.27(0.88)
Total	100	98.62	99.64	99.15	99.98	100.35	99.83
Formula							
Ca	1.00	0.99(0.01)	0.99(0.02)	1.00(0.02)	1.00(0.02)	1.00(0.02)	1.01(0.01)
Ti	1.00	0.99(0.02)	0.99(0.02)	1.03(0.03)	1.01(0.03)	1.01(0.02)	1.00(0.02)
Si	1.00	1.01(0.03)	1.01(0.02)	0.97(0.03)	1.00(0.02)	0.99(0.02)	1.02(0.02)
O	5.00	5.01(0.03)	5.00(0.04)	5.00(0.05)	4.98(0.05)	5.00(0.03)	4.96(0.04)

Note: Numbers in parentheses represent one standard deviation.

the enthalpy and entropy of titanite (Xirouchakis and Lindsley in preparation). Hence, inappropriate values of the first can influence the accepted value of the second.

Motivated by the above observations we used the technique of high-temperature drop-solution calorimetry to measure the enthalpy of drop solution of four carefully characterized synthetic titanite polycrystalline samples and of a stoichiometric glass. The data allowed the standard state enthalpy of formation of stoichiometric, end-member titanite ($CaTiSiO_5$) to be redetermined, and the enthalpy of formation of $CaTiSiO_5$ glass and the enthalpy of vitrification at 25 °C to be obtained.

EXPERIMENTAL PROCEDURES

Synthesis and sample characterization

The samples in this study were synthesized from glasses of $CaTiSiO_5$ composition, and from mechanical mixtures of $CaSiO_3$-TiO_2, and $CaCO_3$-SiO_2-TiO_2. The $CaSiO_3$ used was synthesized from a mechanical mixture of $CaCO_3$ (Alpha lot 050980) and SiO_2 (JM S50389B) respectively dried at 400 °C (4 h) and 1000 °C (30 h) before weighing. Subsequently the $CaCO_3$-SiO_2 mixture was ground in ethanol in an automatic agate mortar for 3 h. The mixture was slowly decarbonated over a period of 24 to 30 h (from 500 to 1000 °C). Then it was reacted at 1100 °C and ground several times until optical examination and powder X-ray diffraction suggested that only wollastonite was present. The final product was stored in a desiccator. Before weighing, $CaSiO_3$ and TiO_2 (JMC 810420) were dried at 1100 °C for 5 and 30 h, and SiO_2 at 1000 °C for 30 h. We prefer a relatively slow rate of decarbonating $CaCO_3$-bearing mixtures to ensure complete degassing and to avoid the formation of unreacted cores of starting materials in $CaSiO_3$ and $CaTiSiO_5$ grains.

The first glass-derived (glass-derived as opposed to subsolidus-derived denotes samples that went through a melting stage although all samples were obtained by annealing at subsolidus conditions) sample (93-1) was synthesized by annealing a glass powder for 48 h at 1100 °C with two cycles of grinding. Backscattered electron imaging and EDS analysis revealed the presence of Ca- and Si-rich, or Si-rich impurities along grain edges. The presence of crystalline impurities in the powder was only resolved with synchrotron powder X-ray diffraction data; one peak at ~4.1 Å (Xirouchakis et al. 1997). Additionally, electron microprobe analysis (details below) shows that, within the standard deviation of the data, the weight percent of Ca, Ti, and O compare well with ideal titanite (Table 1). While it cannot be proved conclusively, Si deficiency is a real possibility for this sample. Therefore, this powder is likely not phase pure and the titanite crystals are possibly nonstoichiometric. The precursor glass (Table 1: glass 93) was obtained by first melting an equimolar mixture of $CaSiO_3$-TiO_2 in a platium crucible at 1400 °C for 16 h. The temperature was dropped to 1000 °C at a set rate of 360 °C/min, after which the sample was taken out of the furnace and quenched in air. The product, a milky white material, was crushed and ground in ethanol in an agate mortar for 2 h. Chips from this powder were mounted on epoxy to be analyzed with the electron microprobe; the rest was used in the synthesis of sample number 93-1. Optical examination using a petrographic microscope suggested that it is isotropic. No crystals were observed although the physical appearance of this glass hints that some crystalline material might be present. However, backscattered electron imaging suggests that it is single phase with no visible compositional inhomogeneities. Furthermore, the analyses indicate that the glass is of the desired composition (Table 1; glass 93). Therefore, if other phases are present then their apparent dimensions have to be less than or close to 1 μm, which is the diameter of the electron beam.

The second glass-derived sample (no. 96-2) was synthesized by recrystallizing a portion of a glass powder (sample no. glass 96) at 1100 °C for 5 d and 24 h at 1050 °C with two cycles of thorough grinding in between. Electron microprobe analyses and optical examination using backscattered electron imaging indicate that the titanite grains are stoichiometric and the powder is phase pure.

Two more samples were obtained by synthesis at subsolidus conditions avoiding entirely a melting stage. The first one (sample no. 95-2) was synthesized by slowly decarbonating a mechanical mixture of $CaCO_3$-TiO_2-SiO_2 from 400 to 1100 °C over a period of several days. As a result titanite as well as perovskite and wollastonite also formed. During decarbonation the mixture was ground in an agate mortar for short but frequent grinding intervals. This was done to minimize the possible introduction of silica from the agate mortar. Nevertheless, it had the equally undesirable result of producing an apparently poorly mixed powder, because even after reaction at 1250 °C for 166 h, powder X-ray diffraction suggested that silica (quartz?) and perovskite still remained as phase impurities. This mixture was reacted at 1100 °C for 15 d with several cycles of grinding (2–3 h) in between to eliminate the unreacted material. However, optical examination during electron microprobe analysis confirmed the presence of silica but not perovskite. From the available data this sample is considered to be stoichiometric with 1–2% SiO_2 and possibly $CaTiO_3$ present as phase impurities.

The second subsolidus-derived titanite (sample no. 96-1) was synthesized by reacting in a platium crucible an equimolar mechanical mixture of $CaSiO_3$-TiO_2 at 1100 °C for 14 d and 1200 °C for 21 d with 2–3 h of grinding between annealing periods. Optical examination during electron microanalysis revealed the presence of several (3–5) grains of $CaSiO_3$ and one grain of SiO_2 as cores in titanite grains. These titanite grains were analyzed and found to have end-member composition. The presence of either $CaSiO_3$ or SiO_2 is suggested because of a weakly diffuse non-titanite peak at ~4.1 Å but only from synchrotron powder X-ray diffraction data. From the available observations this sample is believed to be stoichiometric and virtually phase pure.

The glass sample used for calorimetry (sample no. glass 96) was obtained as follows. First, a $CaCO_3$-TiO_2-SiO_2 mixture was decarbonated by raising the temperature from 500 to 1000 °C over a period of 75 h and at 1050 °C for 3 d. The mixture was then melted in a platimum crucible at 1400 °C for 24 h. Subsequently, it was taken out of the furnace and quickly quenched in water i.e., from red heat to below incandescent temperature within 60 s. The product was a transparent and clear material. The only apparent flaw, observed at the surface of the bulk material and in contact with the platimum crucible, was a small, ≤ 2 mm^2, circular milky white area superficially similar to the previous glass (glass 93). Optical examination and powder X-ray diffraction (Cu$K\alpha$ radiation), before and after drying at 200 °C for 10 h, indicate that it is isotropic and does not contain any crystals. Chips from this glass were also analyzed using an electron microprobe. From the available observations and analyses it is inferred that the glass is homogeneous, pure, and stoichiometric (Table 1, column 4; glass 96). No compositional differences were resolved between the two synthetic glasses. However, the fact that one (sample no. glass 96) is transparent whereas the other (sample no. glass 93) is opaque suggests that they probably differ.

Electron microprobe analysis

The synthetic materials were analyzed with a four-spectrometer CAMEBAX electron microprobe. The analytical conditions were an accelerating voltage of 15 kV, a beam current of 20 nA, a 1 μm beam, and counting times of 60 s with a required precision of 0.3%. Anorthite (USMN 137041) was used as standard for Ca, Si, O, and ilmenite (USMN 96189) for Ti, and titanite (C.M. Taylor Corporation) for Ca, Ti, Si, and O. The O was analyzed using a multi-layered WSi crystal. The carbon-coated surface of the probe mounts and that of a brass cylinder, coated together with the samples, were checked against the surface of a brass cylinder that was coated the same time as the standards. The raw data were reduced with the PAP and ZAF correction routines. No differences were observed. During each electron microprobe analysis session, the standards were also analyzed to check the reproducibility of the standardization. Analyses were accepted if the sum of the weights of the elements was 100 (±2) (Table 1).

Drop solution calorimetry

Five series of drop solution experiments, one for each sample, were performed in a twin Tian-Calvet microcalorimeter (Navrotsky 1977; 1997). Before each series of experiments, the crystalline samples were dried at 700 °C for 1 h. Subsequently, approximately 9–15 mg portions of the crystalline samples were pressed into pellets and dropped from room temperature (24 ± 1 °C) through a long silica-glass tube into 30 g of molten $2PbO \cdot B_2O_3$ contained in a platimum crucible at 702 °C. The measured enthalpy effect is the sum of the enthalpy of solution and the heat content of the sample. The dissolution of the pellets was generally complete within 60 min. The total mass of sample dissolved in lead borate did not exceed 70 mg in each series of experiments (several drops). After completion of each series of drop solution experiments, the lead borate solvent was optically examined to confirm the dissolution of the samples. Additionally, the dissolution of the pellets in the calorimeter was simulated and confirmed by observing the complete dissolution of a 10 mg pellet in 10 g of solvent after 1 h at 702 °C. An average calibration factor, obtained from α-Al_2O_3 calibration of the calorimeter (Kiseleva et al. 1996) over a period of six months, was used to calculate the enthalpies of drop solution.

Attempts at obtaining the enthalpy of drop solution of pellets of the $CaTiSiO_5$ glass showed that they did not dissolve completely under the same conditions used for the crystalline samples. Using smaller pellets (4–6 mg) and a new technique, which bubbles a gas (in this case compressed dry air) through the solvent both to control oxidation state when appropriate and to stir the melt (McHale et al. 1996), we obtained complete dissolution of the glass and reproducible enthalpy effects. Experiments using SiO_2 (glass) and α-Al_2O_3, have shown that results obtained using the bubbling technique may be directly compared with those normally obtained using drop solution with no correction required for any possible effect of bubbling on calorimeter operation or calibration factor.

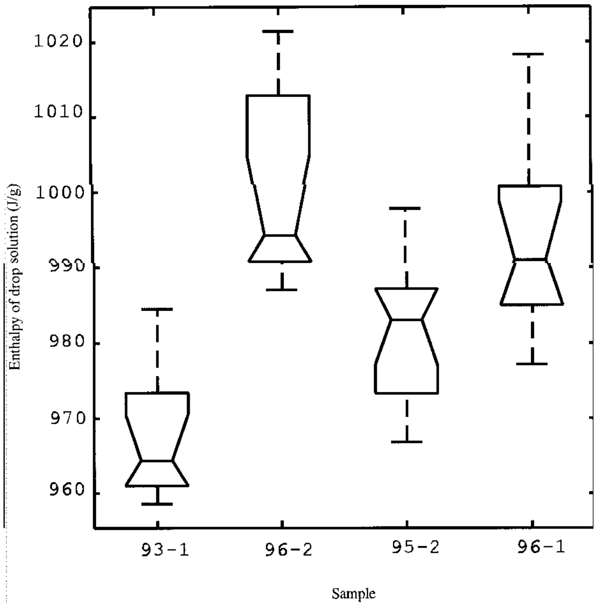

FIGURE 1. Plot of the enthalpy of drop solution (J/g) vs. sample number. The lower and upper lines of each "box" represent the upper and lower quartile of the samples. The intermediate line represents the mean of each sample. The dashed lines outside each box show the range of the data. The notches in the boxes are a graphic confidence interval about the mean of the sample.

TABLE 2. Enthalpy of drop solution of titanite ($CaTiSiO_5$)

Mass (mg)	J/g	kJ/mol
	Glass 96	
4.29	576.04	112.94
5.26	624.44	122.43
4.83	574.66	112.67
5.91	614.5	120.48
6.22	561.15	110.02
5.66	608.22	119.25
6.75	563.9	110.56
6.31	609.14	119.43
4.73	545.69	106.99
6.02	573.49	112.44
5.65	569.92	111.74
7.25	607.31	119.07
6.67	583.9	114.48
Mean	585.57	114.81
2 std error	14.09	2.76
	93-1	
13.52	962.65	188.74
11.28	966.05	189.41
11.14	984.46	193.02
10.5	973.39	190.85
11.45	961.43	188.5
12.31	982.49	192.63
10.28	966.5	189.49
10.44	961.03	188.42
9.51	961	188.42
12.36	958.55	187.94
Mean	967.76	189.74
2 std error	6.18	1.21
	95-2	
11.32	985.38	193.2
10.15	966.81	189.56
12.29	983.06	192.74
11.00	967.26	189.64
12.13	984.73	193.07
12.31	971.75	190.52
13.31	993.96	194.88
13.74	973.81	190.93
12.45	997.85	195.64
11.34	982.94	192.72
9.93	992.59	194.61
10.41	982.1	192.55
12.44	984.54	193.03
Mean	982.06	192.54
2 std error	5.66	1.11
	96-1	
13.38	1000.69	197.42
14.52	1018.20	199.63
14.47	996.42	195.36
14.86	1000.70	197.51
15.97	990.57	194.21
14.08	984.05	192.94
14.81	977.17	191.59
17.27	991.27	194.35
15.86	985.02	193.13
15.81	984.95	193.11
Mean	994.19	194.92
2 std error	8.61	1.69
	96-2	
15.79	990.18	194.14
16.03	1016.6	199.31
14.04	992.20	194.53
15.15	994.30	194.94
14.18	1021.4	200.2
14.69	988.46	193.8
15.21	1001.60	196.37
14.15	987.03	193.52
14.39	1013.00	198.61
15.31	993.45	194.78
15.10	1012.50	198.52
Mean	1001.00	196.25
2 std error	7.96	1.56

RESULTS AND DISCUSSION

The enthalpies of drop solution for the synthetic glass and crystals are given in Table 2. The data for the crystalline samples are also depicted in Figure 1. Negligible to small correlation exists between enthalpies of drop solution and the mass of the pellets as shown by correlation coefficients close to zero. The measured enthalpies range from a minimum of 958.55 to a maximum of 1018.20 J/g or 187.94 to 199.63 kJ/mol with statistically significant overlap only between the populations of samples 96-1 and 96-2. The arithmetic means of each sample population scatter from approximately 970 to 1000 J/g and 190 to 196 kJ/mol (Fig. 1). Furthermore, a two-sample *t* test also suggests that only the means of samples 96-1 and 96-2 have a good chance of being equal; see also Figure 1. For the rest, the probability of being equal is almost zero at the 95% confidence level. These observations correlate with the physical characteristics of the crystalline samples. Thus, it can be inferred that the scatter in the means reflects the relative quality of each sample. For example, if we neglect the possible presence of $CaTiO_3$ in sample 95-2 and also assume that the silica phase present is quartz then the measured enthalpy of drop solution is given by the relation:

$$\Delta H^{\text{measured}}_{\text{Titanite}} = (1 - x)\Delta H^{\text{true}}_{\text{Titanite}} + x\Delta H_{\text{Quartz}}.$$

For $x_{\max} = 0.02$ and $\Delta H_{\text{Qtz}} = 39.1$ kJ/mol (Kiseleva et al. 1996) the corrected enthalpy of drop solution of sample 95-2 is 195.67 ± 0.56 kJ/mol. This may be a maximum

TABLE 3. Thermochemical cycles employed

$CaCo_3$(xl, 298 K) = CaO(sol, 975 K) + CO_2(gas, 975 K)	$\Delta H_1 = 193.4 \pm 0.70$ kJ/mol
CaO(xl, 298 K) + CO_2(gas, 298 K) = $CaCO_3$(xl, 298 K)	$\Delta H_2 = -178.77 \pm 1.00$ kJ/mol
CO_2(gas, 975 K) = CO_2(gas, 298 K)	$\Delta H_3 = -32.06$ kJ/mol
TiO_2(xl, 298 K) = TiO_2(sol, 975 K)	$\Delta H_4 = 54.36 \pm 1.47$ kJ/mol
SiO_2(xl, 298 K) = SiO_2(sol, 975 K)	$\Delta H_5 = 39.1 \pm 0.30$ kJ/mol
CaO(sol, 975 K) + TiO_2(sol, 975 K) + SiO_2(sol, 975 K) = $CaTiSiO_5$(xl, 298 k)	ΔH_6
CaO(sol, 975 K) + TiO_2(sol, 975 K) + SiO_2(sol, 975 K) = $CaTiSiO_5$(gl, 298 k)	ΔH_7
$\Delta_f H^{o,\ xl}_{298,\ oxides} = \Delta H_1 + \Delta H_2 + \Delta H_3 + \Delta H_4 + \Delta H_5 + \Delta H_6$	
$\Delta_f H^{o,\ gl}_{298,\ oxides} = \Delta H_1 + \Delta H_2 + \Delta H_3 + \Delta H_4 + \Delta H_5 + \Delta H_7$	
Ca + ½O_2 = CaO (xl, 298 K)	$\Delta H_8 = -635.089 \pm 0.88$ kJ/mol
Ti + O_2 = TiO_2 (xl, 298 K)	$\Delta H_9 = -944.750 \pm 1.26$ kJ/mol
Si + O_2 = SiO_2 (xl, 298 k)	$\Delta H_{10} = -910.700 \pm 1.00$ kJ/mol
$\Delta_f H^{o,\ xl}_{298,\ elements} = \Delta_f H^{o,\ xl}_{298,\ oxides} + \Delta H_8 + \Delta H_9 + \Delta H_{10}$	
$\Delta_f H^{o,\ gl}_{298,\ elements} = \Delta_f H^{o,\ gl}_{298,\ oxides} + \Delta H_8 + \Delta H_9 + \Delta H_{10}$	

Notes: ΔH_1: $CaCO_3$ (calcite) enthalpy of drop solution; Kiseleva et al. (1996). ΔH_2: $\Delta_f H^o_{298,\ oxides}$ of calcite; Robie et al. (1978). ΔH_3: Heat content of CO_2; Robie et al. (1978). ΔH_4: TiO_2 (Rut) enthalpy of drop solution; R. L. Putnam (unpublished data, Princeton Calorimetry Laboratory). ΔH_5: SiO_2 (Qtz) enthalpy of drop solution; Kiseleva et al. (1996), Chai and Navrotsky (1993). ΔH_6: $CaTiSiO_5$ (solid) enthalpy of drop solution; this study. ΔH_7: $CaTiSiO_5$ (glass) enthalpy of drop solution; this study. ΔH_8: $\Delta_f H^0_{298,\ elements}$ of CaO; Robie et al. (1978). ΔH_9: $\Delta_f H^0_{298,\ elements}$ of TiO_2 (Rut); Robie et al. (1978). ΔH_{10}: $\Delta_f H^o_{298,\ elements}$ of SiO_2 (Qtz); Robie et al. (1978).

value but it is not unrealistic. However, the results from sample 93-1 cannot be treated with the same ease because the phase impurities can be $CaSiO_3$, SiO_2, or both or $CaTiSiO_5$ glass, or glass and crystals. Additionally, this sample may contain ≤0.2% cation vacancies, resulting in an equivalent amount of phase impurities, as estimated from volume data (Xirouchakis et al. 1996; 1997). Hence, the contribution to the measured enthalpy of drop solution of any $CaSiO_3$ or SiO_2 directly related to cation vacancies should be small. The difficulties encountered in observing the phase impurities either optically or by powder X-ray diffraction suggests that the impurity content of this sample is probably low. Nonetheless, the impurity contribution to the measured enthalpy of drop solution can be apparently significant.

It is more likely that $CaTiSiO_5$ glass or wollastonite and not quartz are the predominant phase impurities in this sample. These phases have higher enthalpies of drop solution than quartz (Kiseleva et al. 1996; Chai and Navrotsky 1993). Thus, even if present in small amounts they can affect the measured enthalpy of drop solution. In addition, the fact that the enthalpy of drop solution of this sample is the least endothermic of all the crystalline samples studied also suggests that it is the least stable. This is consistent with nonstoichiometry or with glass being present.

TABLE 4. Enthalpy of formation of titanite ($CaTiSiO_5$) from the oxides and the elements

$\Delta_f H^o_{298,\ oxides}$ (kJ/mol)	$\Delta_f H^o_{298,\ elements}$ (kJ/mol)	Sample
−38.775 ± 3.37	−2529.31 ± 3.84	glass 96*
−118.89 ± 2.51	−2609.42 ± 3.02	96-1†
−116.51 ± 2.21	−2607.04 ± 2.87	95-2‡
−120.22 ± 2.44	−2610.76 ± 3.05	96-2§
−113.71 ± 2.04	−2604.24 ± 2.74	93-1‖
−119.59 ± 2.24	−2610.13 ± 2.90	preferred#
−110.86 ± 1.52	−2601.40 ± 2.38	King et al. 1954**
−112.34 ± 1.05	−2602.84 ± 2.07	Todd & Kelley 1956††

Note: Uncertainties represent two standard errors.
* Clear, pure, stoichiometric.
† Subsolidus-derived, pure, stoichiometric.
‡ Subsolidus-derived, impure, stoichiometric.
§ Glass-derived, pure, stoichiometric.
‖ Glass-derived, impure, Ca, Si deficient?
Average of 96-1 and 96-2.
** Glass-derived.
†† Glass-derived, King et al. 1954 sample.

The standard state enthalpies of formation from the oxides and the elements were calculated following the thermodynamic cycles listed in Table 3. The enthalpies of formation from the oxides and the elements for each sample are given in Table 4. The differences in the heats of drop solution are reproduced in the derived enthalpies of formation. This is emphasized to point out how well the enthalpy of formation given by King et al. (1954) and Todd and Kelley (1956) compares with the most problematic of the samples, 93-1. The purity of the original titanite sample is estimated to be 99% but the nature of the impurities is unknown (King et al. 1954). However, this implies that the originally measured (i.e., heat content, heat capacity, enthalpy of solution) and the subsequently derived standard state properties (i.e., ΔH^0, ΔS^0) are best described by the relation:

$$Y^{\mathrm{true}}_{\mathrm{Titanite}} = [Y^{\mathrm{measured}}_{\mathrm{Titanite}} - x(Y_{\mathrm{defects\ contribution}}]/(1 - x).$$

Hence, the results of the previous studies (King et al. 1954; Todd and Kelley 1956) may be inaccurate. The third-law entropy value depends on whether phase impurities or vacancies dominate the contribution to entropy from defects. As for the enthalpy of formation, the suggested correction points to a more negative value in good agreement with the values obtained in this study from pure and stoichiometric titanite samples.

The physical and other differences between samples 93-1 and 96-2, the similarities between sample 93-1 and the sample of King et al. (1954), and the observations of Xirouchakis et al. (1996; 1997) all suggest that synthesis of titanite by slow crystallization of melts or by annealing of glasses produced by a relatively slow quench may result in samples that are problematic and not representative of ideal titanite. Use of such samples in reversed experiments may affect the determined topologies if phase impurities react first. Moreover, considering that such specimens may contain vacancies, experiments that critically depend on microscopic properties may be affected. Therefore, the older data should be used with caution. We also reiterate that synthesis of stoichiometric samples is most likely to be successful if carried entirely at subsolidus conditions. Synthesis based upon titanite glasses may not result in either pure or stoichiometric samples depending on the apparent quality of the glass. Finally, from the difference between the recommended value for the crystals and the glass the enthalpy of vitrification at 25 °C is estimated to be 80.78 ± 3.59 kJ/mol.

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