Thermochemistry and the enthalpy of formation of synthetic end-member (CaTiSiO₅) titanite

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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·B₂O₃ solvent at 702°C. The enthalpy of formation of stoichiometric, end-member (CaTiSiO₅) 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 CaTiSiO₅ 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