

New experimental value of the enthalpy of fusion of titanite CaTiSiO_5

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The heat capacity C_p of CaTiSiO_5 melt in the temperature range 1685–1843 K, the enthalpy of vitrification of titanite at 298 K and the enthalpy of fusion of titanite at its temperature of fusion 1656 K have been determined from both drop calorimetry measurements between 823 and 1843 K and hydrofluoric acid solution calorimetry measurements at 298 K: $C_p(\text{melt}, 1685\text{--}1843\text{ K}) = 0.2745 \pm 0.0045\text{ kJ mol}^{-1}\text{ K}^{-1}$, $\Delta_{\text{vitr}}H(298\text{ K}) = 81 \pm 2\text{ kJ mol}^{-1}$, and $\Delta_{\text{fus}}H(1656\text{ K}) = 139 \pm 3\text{ kJ mol}^{-1}$. Extensive premelting effect was observed at melting of titanite.

Introduction

Titanite or sphene, CaTiSiO_5 (CaTiOSiO_4), is a sparse yet widely distributed accessory mineral commonly found in metamorphic and igneous rocks and their associated pegmatites (Speer and Gibbs [1]). It belongs to the group of ferroelectric and antiferroelectric titanates (e.g. BaTiO_3) where the electric polarization results from the displacement of the titanium atom from the centre of the $[\text{TiO}_6]$ octahedron (Ghose et al. [2]). Recently, it has been the subject of several structural investigations focused mainly on paraelectric to antiferroelectric phase transition near 500 K (e.g. Ghose et al. [2], Taylor and Brown [3], Zhang et al. [4, 5], Kunz et al. [6], Chrosch et al. [7]). Titanite is known to incorporate a wide variety of impurity ions in solid solution, including actinides and the stable isotopes corresponding to fission products (Vance et al. [8]). Titanite based glass-ceramic materials – titanite crystals in an aluminosilicate glass matrix – are considered as possible hosts for nuclear waste from recycling of nuclear fuel. In recent time several studies have been published examining leach resistance of the titanite glass-ceramic against the ground water and the influence of α - and β -decay on the structure and phase stability of these materials [8, 9, 10, 11, 12].

Zhang et al. [4] observed two weak anomalies in heat capacity of titanite by DSC. The most obvious excess heat capacity occurs near 486 K. It consists of a small λ -shaped anomaly with no visible latent heat. The second anomaly appears as a break in the baseline around 850 K. The effect is very weak.

The low temperature heat capacity of titanite and high temperature heat content of titanite and CaTiSiO_5 melt measured King et al. [13]. However, the description of the sample preparation, given in [13] is quite unclear giving rise to doubts about the phase purity and stoichiometry of the sample used. Xirouchakis et al. [14, 15] studied extensively the correlation between the way of synthesis and lattice parameters of titanite and concluded, that

titanite synthesis by slow crystallisation of stoichiometric melt followed by subsolidus annealing of titanite glass may result in impure, possibly nonstoichiometric samples, that have larger unit cells probably because of vacancies in the Ca, Si, or both sites. By these authors the synthesis of stoichiometric samples is most likely to be successful if carried entirely in subsolidus conditions.

Xirouchakis et al. [14] on the base of drop-solution calorimetry measurements revised the enthalpy of formation of titanite to be $-11.59 \pm 2.24 \text{ kJ mol}^{-1}$ from the oxides and $-2610.13 \pm 2.9 \text{ kJ mol}^{-1}$ from the elements at 298 K. They also determined the enthalpy of formation of CaTiSiO_5 glass to be $-38.775 \pm 3.37 \text{ kJ mol}^{-1}$ from the oxides and $-2529.31 \pm 3.84 \text{ kJ mol}^{-1}$ from the elements and the enthalpy of vitrification of titanite to be $80.78 \pm 3.59 \text{ kJ mol}^{-1}$.

Recently Thiéblot et al. [16] redetermined the heat capacity of crystalline phase between 400 and 1811 K. They have not found any significant calorimetric effect of the para-antiferroelectric transition near 500 K. On the other hand, they confirmed a large premelting effect, found by King et al. [13]. Thiéblot et al. [16] used a sample prepared by crystallisation of stoichiometric melt, with the unit cell parameters consistent with the results reviewed by Xirouchakis et al. [14] for subsolidus-derived samples.

We aimed to redetermine the heat capacities of titanite measured by King et al. [13] and Thiéblot et al. [16], the heat capacity of CaTiSiO_5 melt measured by King et al. [13] and to check the enthalpy of fusion of titanite, determined by King et al. [13].

Experimental methods

Sample preparation

The sample has been produced by temperature controlled slow cooling of the stoichiometric melt and annealing of the glass. Starting materials were CaCO_3 (Specpure, JMC), SiO_2 (Specpure, JMC) and TiO_2 (p.a., 99.5 % Lachema). A stoichiometric mixture was prepared from properly dried components. The mixture was heated 2 h at 950 °C, then 3 h at 1450 °C and further 5 h at 1350 °C followed by slow cooling down to ambient temperature (approximately 10 °C min⁻¹). The phase composition was checked by powder RTG diffraction analysis. No foreign phases were observed in the sample used for calorimetric experiments.

Drop calorimetry

The high temperature drop calorimeter used in this study was described by Proks et al. [17]. About 1 g of a fine powdered sample was loaded in a PtRh 15 % crucible. A PtRh 15 % cover was then welded to the crucible, to prevent leaking of the sample during measurements. The temperature was measured by a thermocouple placed close to the crucible. A temperature difference due to the different positions of the sample and the thermocouple was compensated by a calibration. After having been heated for >1 h at constant temperature the crucible was dropped into a calorimetric copper block, in which the enthalpy released was measured. The cooling of the block was followed 1 h. The heat released after this period was calculated by extrapolation [18].

HF solution calorimetry

An isoperibolic type apparatus, working at 298 K was used. It consists of a Teflon calorimetric vessel with a sample introducing equipment, a sensor for measuring of temperature changes (resistor thermometer), a calibration heating resistor and a mixing device. The calorimetric vessel is placed in surrounding kept at constant temperature. About 50 mg of fine powdered sample is solved in approximately 250 cm³ of a solvent. During the starting period when the stationary state is being achieved the sample is placed in a small container and plunged in the solvent to equilibrate the temperature. The solvent was prepared by mixing of 2 volume parts of 40 % HF with 1 volume part of 36 % HCl diluted with water in the volume ratio 1:1. Each sample was solved in a separate portion of the solvent. Each dissolving experiment was followed by a calibration measurement using heating resistor. The scale of measurable values of enthalpy by the calorimeter is about 100–250 J, the uncertainty of the measurement is about 2–3 J [19].

Results and discussion

Relative enthalpy

The measured enthalpy increments $H(T) - H(298 \text{ K})$ in comparison with values, by King et al. [13] and Thiéblot et al. [16] are plotted in Fig 1. For the crystalline phase an excellent agreement with results of King et al. [13] and Thiéblot et al. [16] was achieved. Similarly as by Thiéblot et al. [16] the enthalpic effects of the phase transitions at 850 K and possibly near 1150 K reported recently by Zhang et al. [5] and Chrosch et al. [7] are not apparent in our relative enthalpy data. They are probably too small to be detected by drop

calorimetry. The best fit with reasonable standard deviations of coefficients in the temperature interval 823–1573 K was achieved by the equation

$$H_{\text{rel}}(\text{cr}, T)/(\text{kJ mol}^{-1}) = (-58.449 \pm 5.266) + (0.1693 \pm 0.0089) T/\text{K} + (1.388 \cdot 10^{-5} \pm 3.66 \cdot 10^{-6}) T^2/\text{K}^2 \quad (1)$$

The standard deviation of the calculated value in the above temperature interval is

$$s(H_{\text{rel}}(\text{cr})) < 1.1 \text{ kJ mol}^{-1}.$$

Considerable premelting effect was observed at melting of titanite. The onset of premelting was observed near 1550 K by King et al. [13] and Thiéblot et al [16]. By our data the premelting effect seems to start at temperatures above 1573 K. Although this estimate is not well constrained because the onset of the premelting and the actual limit between premelting and melting is difficult to determine, the premelting enthalpy must represent a significant part of the enthalpy of fusion.

Heat capacity

Derivation of Equation (1) with respect to temperature gives a linear relation, which returns the heat capacity with relative error less than 3 %.

Enthalpy of cooling of CaTiSiO₅ melt

While in the calorimetric block of the drop calorimeter quite quick cooling of the sample occurs in the case of a liquid sample the product of cooling may be a glass. RTG diffraction showed that this was the case with the studied system. Hence, the measured

enthalpy of cooling of CaTiSiO_5 melt represents an enthalpy change at cooling of the melt from temperature T to a glass at temperature 298 K

$$\Delta_{\text{cool}}H(\text{melt}, T) = H(\text{gl}, 298 \text{ K}) - H(\text{melt}, T) \quad (2)$$

In the temperature interval 1685–1843 K the Equation

$$-\Delta_{\text{cool}}H(\text{melt}, T)/(\text{kJ mol}^{-1}) = (-136,10 \pm 7.75) + (0.2745 \pm 0.0045) T/\text{K} \quad (3)$$

fits the measured data within the standard deviation of the calculated value

$d(\Delta_{\text{cool}}H(\text{melt})) < 1.7 \text{ kJ mol}^{-1}$. Derivation of Equation (3) gives the heat capacity of the CaTiSiO_5 melt independent on temperature:

$$C_p(\text{melt}, 1685\text{--}1843 \text{ K}) = 0.2745 \pm 0.0045 \text{ kJ mol}^{-1} \text{ K}^{-1}. \quad (4)$$

Enthalpy of solution of titanite and CaTiSiO_5 glass

The arithmetic means of experimental enthalpies of solution of titanite and CaTiSiO_5 glass, along with standard deviations are as follows, respectively

$$\Delta_{\text{sol}}H(\text{cr}, 298 \text{ K}) = -377.4 \pm 3.0 \text{ kJ mol}^{-1}$$

$$\Delta_{\text{sol}}H(\text{gl}, 298 \text{ K}) = -458.2 \pm 1.6 \text{ kJ mol}^{-1}$$

The glasses produced during drop calorimetry measurements were used to measure enthalpy of solution. In the frame of the experimental uncertainty the measured data for glasses did not show any significant correlation between the measured enthalpy of solution of glass and the glass history, i.e. the enthalpy of solution did not depend on temperature from which the melt was quenched in the drop calorimeter.

Enthalpy of vitrification of titanite

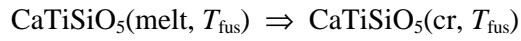
The enthalpy of vitrification at 298 K determined as a difference between the enthalpy of solution of crystalline phase and of CaTiSiO₅ glass

$$\Delta_{\text{vitr}}H(298 \text{ K}) = \Delta_{\text{sol}}H(\text{cr}, 298 \text{ K}) - \Delta_{\text{sol}}H(\text{gl}, 298 \text{ K}) \quad (5)$$

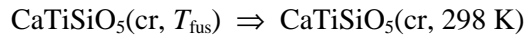
was determined to be $81 \pm 3.4 \text{ kJ mol}^{-1}$. This value is in excellent agreement with previously published value $80.78 \pm 3.59 \text{ kJ mol}^{-1}$ by Xirouchakis et al. [14].

Enthalpy and entropy of fusion of titanite

The enthalpy of congruent fusion of titanite at its temperature of fusion has been determined using relative enthalpy of titanite at this temperature with respect to a reference state of the crystalline phase at 298 K ($H_{\text{rel}}(\text{cr}, T_{\text{fus}})$), using enthalpy of CaTiSiO₅ melt at temperature of fusion of titanite referred to a state of the CaTiSiO₅ glass at 298 K ($\Delta_{\text{cool}}H(\text{melt}, T_{\text{fus}} \rightarrow \text{gl}, 298 \text{ K})$) and using the enthalpy of vitrification of titanite at 298 K on the base of the following thermodynamic cycle:



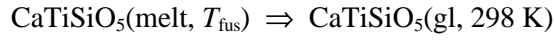
$$\Delta_{\text{cryst}}H(\text{melt}, T_{\text{fus}}) \equiv -\Delta_{\text{fus}}H(\text{cr}, T_{\text{fus}})$$



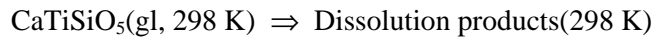
$$\Delta_{\text{cool}}H(\text{cr}, T_{\text{fus}} \rightarrow 298 \text{ K}) \equiv -H_{\text{rel}}(\text{cr}, T_{\text{fus}})$$



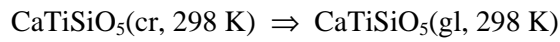
$$\Delta_{\text{sol}}H(\text{cr}, 298 \text{ K})$$



$$\Delta_{\text{cool}}H(\text{melt}, T_{\text{fus}} \rightarrow \text{gl}, 298 \text{ K})$$



$$\Delta_{\text{sol}}H(\text{gl}, 298 \text{ K})$$



$$\Delta_{\text{vitr}}H(\text{cr}, 298 \text{ K}) \equiv H_{\text{rel}}(\text{gl}, 298 \text{ K})$$

$$\Delta_{\text{fus}}H(T_{\text{fus}}) = \Delta_{\text{cool}}H(\text{cr}, T_{\text{fus}} \rightarrow 298 \text{ K}) + \Delta_{\text{sol}}H(\text{cr}, 298 \text{ K}) - \Delta_{\text{cool}}H(\text{melt}, T_{\text{fus}} \rightarrow \text{gl}, 298 \text{ K}) -$$

$$\Delta_{\text{sol}}H(\text{gl}, 298 \text{ K}) \quad (6)$$

or

$$\Delta_{\text{fus}}H(T_{\text{fus}}) = \Delta_{\text{cool}}H(\text{cr}, T_{\text{fus}} \rightarrow 298 \text{ K}) - \Delta_{\text{cool}}H(\text{melt}, T_{\text{fus}} \rightarrow \text{gl}, 298 \text{ K}) + \Delta_{\text{vitr}}H(298 \text{ K}) \quad (7)$$

Values of enthalpies $\Delta_{\text{cool}}H(\text{cr}, T_{\text{fus}} \rightarrow 298 \text{ K})$ and $\Delta_{\text{cool}}H(\text{melt}, T_{\text{fus}} \rightarrow \text{gl}, 298 \text{ K})$ at the temperature of fusion of titanite have been extrapolated using the temperature dependencies of relative enthalpies of titanite (Eq. 1) and CaTiSiO_5 melt (Eq. 3), respectively, to the temperature of fusion. The temperature of fusion 1656 K has been accepted. The determined enthalpy of fusion in comparison with the value measured by King et al. [13] is in Table 1.

Conclusion

The considerable difference between the enthalpy of fusion of titanite determined in this work and the value by King et al. [13] is due to different relative enthalpies of CaTiSiO_5

melt measured in both works. King et al. [13] was able to measure the enthalpy of the melt referred to the state of the crystalline titanite directly. He did not mention any possible production of glass at cooling of the melt. Nevertheless, according to our experience the CaTiSiO_5 glass is produced even in the conditions similar to that, described by King et al. [13] at the synthesis of his crystalline titanite. The formation of glass during the calorimetric experiment, similarly as in our case, could be the reason for the lower value of the enthalpy of cooling of melt determined by King et al. [13].

On the other hand, as mentioned above, Xirouchakis et al. [14, 15] has pointed out, that lattice parameters and phase purity of titanite may depend on synthesis conditions. Although the heat capacities are in general less sensitive to mirror structural differences and nonstoichiometry of the sample [14], the enthalpies of solution may reflect these properties very sensitively. That is why we can not exclude, that discrepancy between both experimental values of the enthalpy of fusion is due to the small differences in sample properties caused by the conditions of the synthesis of both crystalline samples.

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Figure caption

Figure 1. Experimental enthalpies of titanite.

Table

Table. 1. Comparison of the enthalpies and entropies of fusion of titanite

	$T_{\text{fus}} / \text{K}$	$\Delta_{\text{fus}}H (T_{\text{fus}}) / (\text{kJ mol}^{-1})$	$\Delta_{\text{fus}}S (T_{\text{fus}}) / (\text{J mol}^{-1}\text{K}^{-1})$
This work	1653–1658	139 ± 4	84 ± 2.4
King et al. [13]	1670	123.9	74.19
Thiéblot et al. [16]	1658 ± 3		
Pelton [21]	1657		
De Vries [20]	1655		

