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Thermodynamic properties of calcium titanates: $CaTiO_3$, $Ca_4Ti_3O_{10}$, and $Ca_3Ti_2O_7$

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The chemical potentials of CaO in two-phase fields ($TiO_2 + CaTiO_3$), ($CaTiO_3 + Ca_4Ti_3O_{10}$), and ($Ca_4Ti_3O_{10} + Ca_3Ti_2O_7$) of the pseudo-binary system (CaO + TiO_2) have been measured in the temperature range (900 to 1250) K, relative to pure CaO as the reference state, using solid-state galvanic cells incorporating single crystal CaF_2 as the solid electrolyte. The cells were operated under pure oxygen at ambient pressure. The standard Gibbs free energies of formation of calcium titanates, $CaTiO_3$, $Ca_4Ti_3O_{10}$, and $Ca_3Ti_2O_7$, from their component binary oxides were derived from the reversible e.m.f.s. The results can be summarised by the following equations: $CaO(solid) + TiO_2(solid) \rightarrow CaTiO_3(solid)$, $\Delta G^\circ \pm 85/(J \cdot mol^{-1}) = -80{,}140 - 6.302(T/K)$; $4CaO(solid) + 3TiO_2(solid) \rightarrow Ca_4Ti_3O_{10}(solid)$, $\Delta G^\circ \pm 275/(J \cdot mol^{-1}) = -243{,}473 - 25.758(T/K)$; $3CaO(solid) + 2TiO_2(solid) \rightarrow Ca_3Ti_2O_7(solid)$, $\Delta G^\circ \pm 185/(J \cdot mol^{-1}) = -164{,}217 - 16.838(T/K)$.

The reference state for solid TiO_2 is the rutile form. The results of this study are in good agreement with thermodynamic data for $CaTiO_3$ reported in the literature. For $Ca_4Ti_3O_{10}$ Gibbs free energy of formation obtained in this study differs significantly from that reported by Taylor and Schmalzried at $T = 873$ K. For $Ca_3Ti_2O_7$ experimental measurements are not available in the literature for direct comparison with the results obtained in this study. Nevertheless, the standard entropy for $Ca_3Ti_2O_7$ at $T = 298.15$ K estimated from the results of this study using the Neumann–Koop rule is in fair agreement with the value obtained from low-temperature heat capacity measurements.

1. Introduction

Thermodynamic data on calcium titanates are of considerable interest in geology, metallurgy and ceramics. Phase equilibria in the pseudo-binary system (CaO + TiO_2) have been studied extensively and the existence of three stable ternary oxides $CaTiO_3$, $Ca_4Ti_3O_{10}$, and $Ca_3Ti_2O_7$ has been established in the literature [1–2]. The three inter-oxide compounds can be visualized as members of the Ruddlesden–Popper series having the general formula $Ca_{n+1}Ti_nO_{3n+1}$, with $n = 2$ for $Ca_3Ti_2O_7$, $n = 3$ for $Ca_4Ti_3O_{10}$, and $n = \infty$ for $CaTiO_3$. The orthorhombic structure of $CaTiO_3$ (space group *Pcmn*) results from the tilting of TiO_6 octahedra with respect to the cubic perovskite axes. In $Ca_3Ti_2O_7$ and $Ca_4Ti_3O_{10}$, excess Ca cations are structurally accommodated by regular insertion of distorted NaCl-type layers between perovskite blocks; structure of $Ca_3Ti_2O_7$ consists of double perovskite layers interleaved with CaO, while $Ca_4Ti_3O_{10}$ has triple perovskite layers interleaved with CaO. Preparation of several metastable compositions ($CaTi_2O_5$, $Ca_2Ti_5O_{12}$, and $CaTi_4O_9$) in the pseudo-binary system (CaO + TiO_2) have been reported in the literature [3–6]. They decompose to the stable phases when heated at $T > 1073$ K.

Significant amount of thermodynamic data are available in the literature for the compound $CaTiO_3$. Shomate [7] has reported low-temperature heat capacities of $CaTiO_3$ from (50 to 300) K. More recently Woodfield *et al.* [8] have extended these measurements from (15 to 400) K using an adiabatic calorimeter. High-temperature enthalpy data have been reported by Naylor and Cook [9] and Guyot *et al.* [10]. The results of Guyot *et al.* are lower by ~ 1 per cent than the earlier results of Naylor and Cook below $T = 1100$ K. Guyot *et al.* [10] report two phase transitions missed by Naylor and Cook, one at $T = 1384$ K and the other at $T = 1520$ K. Four independent measurements of the standard enthalpy of formation of $CaTiO_3$ from its component binary oxides CaO and TiO_2 are available. Kelly *et al.* [11] used aqueous acid solution calorimetry to derive a value of $(-81.01 \pm 1.04)\ kJ \cdot mol^{-1}$ at $T = 298.15$ K. Muromachi and Navrotsky [12] used high-temperature oxide-melt solution calorimetry with lead borate ($Pb_2B_2O_5$) as solvent to obtain a value of $(-80.9 \pm 2.3)\ kJ \cdot mol^{-1}$ at $T = 1068$ K. Putnam *et al.* [13] have used the same lead borate solvent to derive values of $(-77.46 \pm 2.4)\ kJ \cdot mol^{-1}$ at $T = 973$ K and $(-84.72 \pm 2.9)\ kJ \cdot mol^{-1}$ at $T = 1046$ K. Determined by Panfilov and Feodosev [14] using bomb calorimeter was the enthalpy change for the reaction, $CaCO_3(solid) + TiO_2(solid) \rightarrow CaTiO_3(solid) + CO_2(gas)$. The standard enthalpy of formation of $CaTiO_3$ from elements at $T = 298.15$ K derived from this measurement was $(-1662.7 \pm 5)\ kJ \cdot mol^{-1}$.

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Combining this with data for CaO and TiO_2 from JANAF tables [15], the enthalpy of formation from component binary oxides is obtained as $(-82.88 \pm 7)\ kJ \cdot mol^{-1}$, in good agreement with solution calorimetric data [11–13]. Based on the available calorimetric data, Woodfield *et al.* [8] have composed a self-consistent set of thermodynamic properties for $CaTiO_3$ up to $T = 1900$ K. Using a solid-state electrochemical cell based on CaF_2 as the electrolyte, Taylor and Schmalzried [16] determined the Gibbs free energies of formation of $CaTiO_3$ at $T = 873$ K, and $Ca_4Ti_3O_{10}$ at $T = 813$ K.

Enthalpy and Gibbs free energy of formation of $Ca_3Ti_2O_7$ have not been measured. The standard entropy of $Ca_3Ti_2O_7$ at 298.15 K has been calculated from low-temperature heat capacity measurement of King [17] in the temperature range (51 to 298) K. The heat capacity of $Ca_4Ti_3O_{10}$ has not been measured. The purpose of this study was to determine standard Gibbs free energies of formation of $Ca_3Ti_2O_7$ as a function of temperature. The measurement procedure also generates values for $CaTiO_3$ and $Ca_4Ti_3O_{10}$ which provide a check on data in the literature. The solid-state cells used in this study essentially measure the chemical potential of CaO, relative to pure CaO as the standard state, in the two-phase regions of the pseudo-binary system $(CaO + TiO_2)$ in pure oxygen. The standard Gibbs free energies of formation of the three stable titanates from their component binary oxides are calculated as a function of temperature from the measured chemical potentials of CaO.

2. Experimental methods

2.1. Materials

The starting materials were $CaCO_3$ and TiO_2 (rutile type) of mass fraction purity >0.9999. Calcium titanates, $CaTiO_3$, $Ca_4Ti_3O_{10}$, and $Ca_3Ti_2O_7$, were prepared by heating mixtures of CaO and TiO_2 in the appropriate molar ratio contained in platinum crucibles at $T = 1773$ K for 160 ks in air with three intermediate grindings. A reactive form of CaO, obtained by decomposition of $CaCO_3$ in vacuum ($p \approx 10$ Pa) at $T = 1100$ K, was used in the preparation of ternary oxides. The rutile form of TiO_2 was dried at $T = 573$ K before use. The mixtures of component oxides were pelletized at $p = 100$ MPa using a steel die before heating. Completion of the reaction was confirmed by powder X-ray diffraction (XRD) analysis of the product. All the three titanates had the orthorhombic structure: $CaTiO_3$ with cell parameters $a = 0.5441$ nm, $b = 0.7642$ nm, and $c = 0.5380$ nm; $Ca_4Ti_3O_{10}$ with cell parameters $a = 0.5408$ nm, $b = 2.7143$ nm, and $c = 0.5434$ nm; $Ca_3Ti_2O_7$ with cell parameters $a = 0.5417$ nm, $b = 1.9517$ nm, and $c = 0.5423$ nm. Transparent single crystals of CaF_2 for use as solid electrolytes were obtained in the form of disks, 1.5 cm in diameter and 0.3 cm thick. The high-purity oxygen gas, used to fix the oxygen potential over the electrodes of the solid-state cell, was passed through sodium hydroxide to remove traces of CO_2 and then dried by passing through columns containing anhydrous magnesium perchlorate and phosphorus pentoxide.

2.2. Apparatus and procedure

The reversible e.m.f. of three solid-state cells,

$$\mathrm{Au, O_2,\ CaO + CaF_2/CaF_2/CaF_2 + CaTiO_3 + TiO_2, O_2, Au,} \tag{I}$$

$$\mathrm{Au, O_2,\ CaO + CaF_2/CaF_2/CaF_2 + Ca_4Ti_3O_{10} + CaTiO_3, O_2, Au,} \tag{II}$$

$$\mathrm{Au, O_2,\ CaO + CaF_2/CaF_2/CaF_2 + Ca_3Ti_2O_7 + Ca_4Ti_3O_{10}, O_2, Au} \tag{III}$$

were measured as a function of temperature in the range (900 to 1250) K. The cells are written such that the right-hand electrodes are positive. The reference electrode consisted of an intimate equimolar mixture of CaO and CaF_2. The mixture was pelletized at $p = 100$ MPa using a steel die and sintered in a stream of prepurified oxygen at $T = 1300$ K. The measuring electrodes consisting of three-phase mixtures of $CaF_2 + CaTiO_3 + TiO_2$, $CaF_2 + Ca_4Ti_3O_{10} + CaTiO_3$, and $CaF_2 + Ca_3Ti_2O_7 + Ca_4Ti_3O_{10}$ in the molar ratio 0.5:1:1 were also pelletized and sintered under identical conditions. Minor variation in the mixing ratio of the constituents forming the electrode did not affect the cell e.m.f. The presence of CaF_2 in the electrode pellets was found necessary to generate fluorine chemical potentials at the electrodes. Since fluorine ions are the mobile species in the CaF_2 solid electrolyte, the cells respond to the difference in fluorine chemical potential at the two electrodes.

A schematic diagram of the apparatus used in this study for electromotive force (e.m.f.) measurements is shown in figure 1. It is similar to those described elsewhere [18,19]. Only some additional details and critical points required for evaluation of the experiments are given here. The electrode pellets were spring-loaded on either side of transparent single crystal CaF_2 electrolyte with a gold mesh sandwiched between each electrode pellet and the electrolyte. Gold electrical leads were spot-welded to the mesh. The presence of the gold catalyst at the electrolyte–electrode interface was found necessary to obtain reproducible e.m.f. Without the catalyst, the e.m.f. of the cell was found to be lower than the equilibrium value, especially at lower temperatures, and the response significantly slower. The pellets were held together under pressure by a system of alumina tubes and rods as shown in the figure. Au foils were placed to prevent physical contact between the electrode pellets and alumina rods and tubes used for holding the pellets under pressure. The cell was enclosed in an outer impervious alumina tube, closed at both ends with brass caps, which had provision for gas inlet and outlet, and electrode and thermocouple leads. The alumina tube was suspended in a vertical resistance furnace. The cell was situated in the even-temperature zone (±1 K) of the furnace. A Faraday cage made of stainless steel foil was placed between the alumina tube and the furnace. The foil was earthed to minimize induced e.m.f. on cell leads from furnace winding.

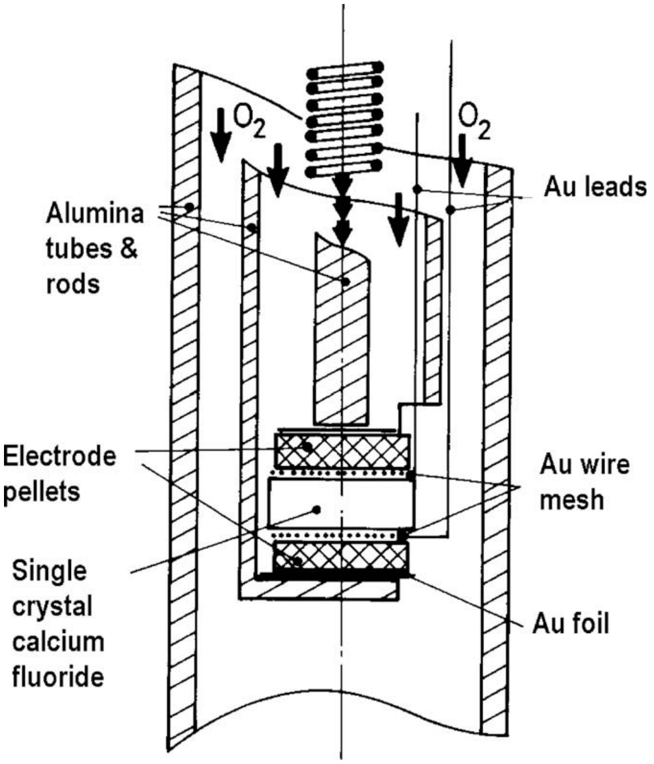

FIGURE 1. Schematic diagram of the apparatus used for emf measurement.