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Thermodynamic properties of $CaTiF_5(s)$

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Abstract

Calcium titanofluoride $CaTiF_5(s)$ was prepared by solid-state reaction of $CaF_2(s)$ with $TiF_3(s)$ and characterized by X-ray diffraction method. The standard molar isobaric heat capacity ($C^\circ_{p,m}$) of $CaTiF_5(s)$ was determined by a power compensated differential scanning calorimeter in the temperature from 230 K to 710 K. A solid-state galvanic cell with CaF_2 as electrolyte was used to determine the standard molar Gibbs energy of formation ($\Delta_f G^\circ_m$) of $CaTiF_5$ in the temperature range from 803 K to 1005 K. The galvanic cell can be depicted as:

$$(-)\text{Pt,O}_2(\text{g,101.325 kPa})/\{\text{CaO(s)} + \text{CaF}_2(\text{s})\}//\text{CaF}_2//\{\text{CaTiF}_5(\text{s}) + \text{CaTiO}_3(\text{s})\}/\text{O}_2(\text{g,101.325 kPa}), \text{Pt}(+)$$

The second law analysis of present data were carried out to derive the standard entropy $S^\circ_m(298.15\text{ K})$ and the enthalpy of formation $\Delta_f H^\circ_m(298.15\text{ K})$ and the values derived are $68.7\text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ and $-2848.4\text{ kJ}\cdot\text{mol}^{-1}$, respectively.

Keywords: Calcium titanofluoride; Heat capacity; Gibbs energy of formation; Differential scanning calorimetry; Solid-state galvanic cell

1. Introduction

Ternary fluorides with general formula ABF_5 (where A = alkaline earth metal and B = transition metal) are interesting low-dimensional magnetic systems [1–6]. All these compounds are characterized by the presence of isolated chains of magnetic ions $(BF_5)_n^{2n-}$ [6]. Synthesis, crystal structure and magnetic susceptibility measurements on $CaTiF_5(s)$ and $BaTiF_5(s)$ have been carried out by Eicher and Greedan [6], in order to establish a model system for studying low dimensional magnetic interactions involving $(BF_5)_n^{2n-}$ chains. According to Eicher and Greedan [6], $CaTiF_5$ is isostructural with $CaCrF_5$ with monoclinic unit cell and space group *I*2/*c*. Ternary fluorides of alkaline earth metal and transition metals are also considered potentially stable compounds which may form in metallurgical processes where hydrofluoric acid or fluorine environment is used. Knowledge of thermodynamic stabilities of these ternary fluorides is important to predict their formation in different chemical environment. In this study, the thermodynamic properties of $CaTiF_5(s)$ have been investigated by using differential scanning calorimetry and solid-state electrochemical cell methods.

2. Experimental

2.1. Materials preparation

All the starting materials used in this study are supplied by Alfa Aesar, USA with 99.9% metal basis purity, except TiF_3 (purity level not known). Calcium titanofluoride $CaTiF_5(s)$ was prepared by solid-state reaction route. High purity $CaF_2(s)$ and $TiF_3(s)$ were dried in a flow of high purity argon gas atmosphere at $T = 400$ K and stoichiometric proportions were mixed thoroughly in an agate mortar inside an argon atmosphere glove box. The mixture was compacted in to pellet at 20 MPa pressures using a steel

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die and encapsulated in nickel foil and sealed in a quartz ampoule under reduced pressure of 10^{-6} MPa. The quartz ampoule was initially heated from $T = (573$ to $973)$ K with a step of 100 K and 24 h heating at each isothermal step followed by final heating at $T = 1050$ K for 120 h. The ampoule was furnace cooled.

Calcium titanate $CaTiO_3$(s) was prepared by solid-state reaction of CaO(s) and TiO_2(s). Stoichiometric amounts of preheated CaO(s) and TiO_2(s) were thoroughly mixed inside the argon atmosphere glove box and compacted into pellet at 20 MPa pressure using a steel die and heated in an alumina boat at $T = 1723$ K for 120 h with two intermediate grindings.

The products were identified by X-ray diffraction method using a PHILIPS X-ray diffractometer with Cu Kα radiation and graphite monochromator. The powder XRD patterns of $CaTiF_5$(s) and $CaTiO_3$(s) synthesized in this study matched well the JCPDS patterns (File Nos. 77-1526 and 77-0182, respectively) and shown in figure 1. Identification of diffraction pattern for $CaTiF_5$(s) did not show any peaks due to component binary fluorides suggesting complete reaction to form the pure product. Similarly, in the case of $CaTiO_3$(s), diffraction peaks due to component binary oxides were not observed. This ensured that the products are pure phases or the impurities phases present are below the detection limit of the X-ray diffraction instrument used. A powder sample of $CaTiF_5$(s) was used for heat capacity measurements. Based on the phase relations, phase mixtures $\{CaO(s) + CaF_2(s)\}$, $\{MgO(s) + MgF_2(s)\}$, and $\{CaTiF_5(s) + CaTiO_3(s)\}$ were mixed homogenously and pelletised using a steel die at a pressure of 20 MPa and sintered at $T = 973$ K in purified oxygen gas for 24 h which were subsequently used for e.m.f. measurements.

2.2. Differential scanning calorimetric (d.s.c.) measurement

A power compensated d.s.c. (Model: Diamond DSC, Perkin–Elmer) was used for the measurement of heat capacity of $CaTiF_5$(s). The calorimeter has provision for measurement from $T = (223$ to $823)$ K. The temperature and heat flow calibration of the calorimeter were carried out by using the phase transition temperature and enthalpy of phase transition of NIST (National Institute of Standards and Technology) reference materials (biphenyl: $T_{fus} = 342.410$ K, $\Delta_{fus}H = 120.4$ J · g^{-1}; indium: $T_{fus} = 429.748$ K, $\Delta_{fus}H = 28.5$ J · g^{-1}; tin: $T_{fus} = 505.078$ K, $\Delta_{fus}H = 60.2$ J · g^{-1}; and zinc: $T_{fus} = 692.677$ K, $\Delta_{fus}H = 111.2$ J · g^{-1}). The standard molar heat capacity of NIST synthetic sapphire (SRM 720) in the powder form was measured to check the accuracy of measurements and found to be within ±1% of the literature values in the temperature range from $T = (223$ to $773)$ K.

Heat capacity measurements were carried out in two different temperature ranges: (i) $223 \leqslant T/K \leqslant 473$, and (ii) $373 \leqslant T/K \leqslant 773$ at a heating rate of 10 K · min^{-1} with high purity nitrogen as a carrier gas at a flow rate of 5 dm^3 · h^{-1}. The standard ASTM method (ASTM E 1269) [7] was used to calculate the heat capacity of sample. This method requires three measurements with identical temperature program, including isothermal segments at the beginning and the end. The first measurement is a baseline run made with empty crucibles. In the second measurement, a standard reference material (synthetic sapphire, SRM 720) is kept in the sample crucible with reference crucible empty and the third measurement is made with an actual sample in the sample crucible with the reference crucible empty. The three measured signals are corrected

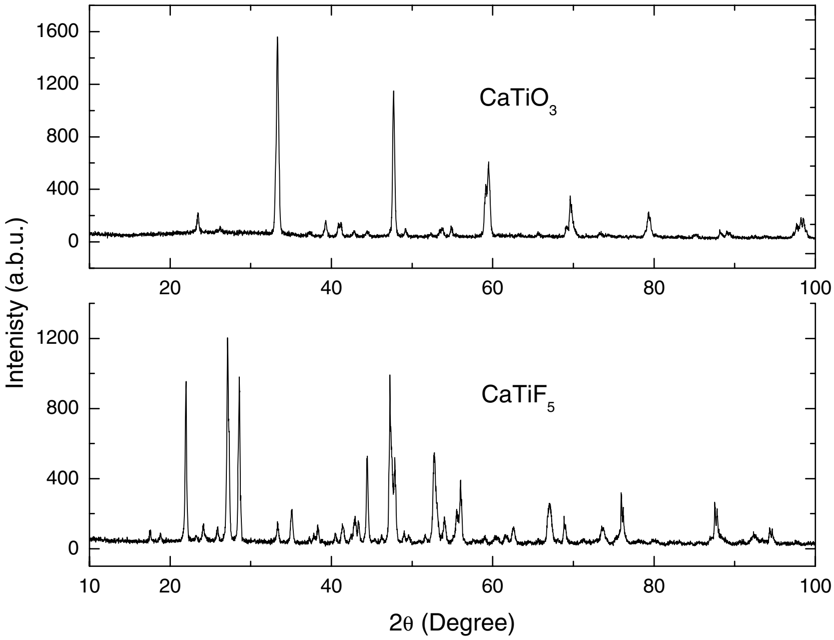

FIGURE 1. X-ray diffraction patterns of $CaTiF_5$(s) and $CaTiO_3$(s).