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Gibbs energy of formation of orthorhombic $CaZrO_3$

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Abstract

The Gibbs free energy of formation of the orthorhombic form of $CaZrO_3$(o) from monoclinic ZrO_2(m) and periclase CaO(p) has been determined as a function of temperature in the range 950–1225 K, using an electrochemical cell incorporating single-crystal CaF_2 as the solid electrolyte. The results are corrected for the small solid solubility of CaO in ZrO_2. For the reaction, $ZrO_2(m) + CaO(p) \rightarrow CaZrO_3(o)$, $\Delta G^\circ = -31\,590 - 13.9T(\pm 180)$ J mol^{-1}.

The "second-law" enthalpy of formation of $CaZrO_3$ obtained from the results of this study at a mean temperature of 1090 K is in excellent agreement with the high-temperature solution calorimetric measurements of Muromachi and Navrotsky at 1068 K (J. Solid State Chem., 72 (1988) 244), and the average value of the bomb and acid solution calorimetric studies of Lvova and Feodosev (Zh. Fiz. Khim., 38 (1964) 28), Korneev et al. (Izv. Akad. Nauk SSSR, Neorg. Mater., 7 (1971) 886) and Brown and Bennington (Thermochim. Acta, 106 (1986) 183). The standard entropy of $CaZrO_3$(o) at 298.15 K from the free energy data is 96.4 ($\pm$3.5) J K^{-1} mol^{-1}. The results of this study are discussed in comparison with high-temperature e.m.f. measurements reported in the literature on cubic zirconia solid solutions.

INTRODUCTION

Zirconia–calcia solid solutions with fluorite structure are known to be good oxygen-ion conductors and have been extensively used in high-temperature sensors [1] and thermodynamic measurements [2] over the past three decades. The activity of CaO in the zirconia-rich solid solution has been measured independently as a function of composition and temperature by Pizzini and Morlotti at 1173–1373 K [3] and by Levitskii et al. at 1200–1450 K [4], using solid state electrochemical cells. According to the phase diagram for the system ZrO_2–CaO [5], solid solution with fluorite structure is not stable in the composition and temperature range covered in the e.m.f. studies [3, 4]. The solid solution should have decomposed gradually to a mixture of tetragonal zirconia solid solution and $CaZrO_3$ below 1397 K [5],

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and to different two-phase mixtures at higher temperatures depending on the composition. In the pseudo-binary system ZrO_2–CaO, there are three stable solid phases: $CaZrO_3$, $CaZr_4O_9$ (ϕ_1) and $Ca_6Zr_{19}O_{44}$ (ϕ_2). It is generally recognized that $CaZrO_3$ with perovskite structure exists in two polymorphic forms: the low-temperature orthorhombic phase and the high-temperature cubic phase, with a transition at 2173 ± 50 K [5]. The ordered compound ϕ_1 is stable only between 1397 and 1509 K [5]. The second ordered compound ϕ_2 exists between 1410 and 1626 K [5].

Recent transport and e.m.f. measurements have indicated that $CaZrO_3$ is also an excellent oxygen-ion conductor and can be used over a wide range of temperature and partial pressure of oxygen for prolonged periods [6]. Unlike ZrO_2–CaO solid solutions, it does not suffer from 'ageing' caused by slow phase transformation at temperatures below 1413 K. Because of the new prominence of $CaZrO_3$ as an ionic conductor, its standard Gibbs energy of formation has been measured using a high-temperature electrochemical technique. The enthalpy of formation of $CaZrO_3$ has been determined by Lvova and Feodosev [7] and Korneev et al. [8] using combustion calorimetry, by Brown and Bennington [9] using acid (HF) solution calorimetry at room temperature, and by Muromachi and Navrotsky [10] using oxide-melt solution calorimetry at 1068 K. The low-temperature heat capacity of $CaZrO_3$ has been measured by King and Weller [11]. The high-temperature enthalpy has been measured by Mezaki et al. [12] at 300–1050 K, by Gvelesiani et al. [13] at 298–1500 K, and by Saha et al. [14] at 1100–1700 K. The Gibbs energy of formation of $CaZrO_3$ has not previously been measured.

EXPERIMENTAL METHODS

Principle

The standard Gibbs free energy of formation of $CaZrO_3$ can be determined using a solid state galvanic cell incorporating single-crystal CaF_2 as the solid electrolyte. The cell can be represented as:

$$\mathrm{Pt,O_2,CaO + CaF_2|CaF_2|CaF_2 + CaZrO_3 + ZrO_2,O_2,Pt} \qquad \text{(cell I)}$$

The cell is written such that the right electrode is positive. The electrochemical reaction at the right electrode is

$$\mathrm{CaF_2 + 2e^- + 0.5O_2 + ZrO_2 \rightarrow CaZrO_3 + 2F^-} \qquad (1)$$

The corresponding reaction at the left electrode is

$$\mathrm{2F^- + CaO \rightarrow CaF_2 + 0.5O_2 + 2e^-} \qquad (2)$$

When the pressures of oxygen at the two electrodes are identical, the virtual cell reaction, obtained by combining the two electrode reactions, can be represented by the equation

$$\mathrm{CaO(p)} + \mathrm{ZrO_2(m)} \rightarrow \mathrm{CaZrO_3(o)} \tag{3}$$

where (o) denotes orthorhombic, (m) monoclinic and (p) periclase structure. The crystal structures of the oxides are identified to avoid ambiguity. The transport number of the fluorine ions in the CaF_2 solid electrolyte is greater than 0.99 at the fluorine chemical potentials prevailing at the two electrodes of cell I [15, 16]. The mutual solubility between CaF_2 and the oxides CaO and ZrO_2 is negligible at the experimental temperatures [17]. However, there is a small solubility of CaO (< 3 mol%) in ZrO_2 [5]. A small correction for the reduction in the activity of ZrO_2 in equilibrium with $CaZrO_3$ is therefore necessary. The standard free energy charge ($\Delta G_3^\ominus$) for reaction (3) can be obtained from the e.m.f. (E)

$$\Delta G_3^\ominus = -\eta FE + RT \ln a_{\mathrm{ZrO_2}} \tag{4}$$

where $\eta = 2$ is the number of electrons associated with the electrode reactions, F is the Faraday constant, and the activity of ZrO_2, $a_{\mathrm{ZrO_2}}$, is approximated by its mole fraction in accordance with Raoult's law.

In the design of galvanic cells for thermodynamic measurements, it is important to eliminate side reactions. A possible displacement reaction at the right electrode is

$$2\mathrm{CaF_2} + \mathrm{ZrO_2} \rightarrow \mathrm{ZrF_4} + 2\mathrm{CaO} \tag{5}$$

Because the standard free energy change for this reaction has a large positive value (377.89 kJ mol^{-1} at 1100 K) [18], it is unlikely to affect the e.m.f. measurement.

Materials

For the electrolyte, optical-grade single crystals of CaF_2 in the form of discs 1.5 cm in diameter and 0.2 cm thick, were obtained from the Harshaw Chemical Company. Ultrapure anhydrous CaF_2 (99.999%) powder was supplied by the Apache Chemical Company. The oxygen gas used was 99.999% pure and was dried by passing through columns of silica gel, anhydrous $Mg(ClO_4)_2$ and P_2O_5. The flow rate of oxygen was set by a mass flow controller.

The compound $CaZrO_3$ was prepared by the solid state reaction of a mixture of high purity $CaCO_3$ and ZrO_2. Precisely measured stoichiometric amounts of -270 mesh $CaCO_3$ and ZrO_2 were blended and compacted in a large Pt dish. The mixture was heated slowly to 800 K and then to 1250 K over a period of 120 ks to ensure decomposition of $CaCO_3$ and initial reaction, with ZrO_2. The product was ground to -270 mesh, recompacted and heated at 1500 K for 300 ks. The procedure was repeated twice. X-ray diffraction analysis indicated that the product was orthorhombic $CaZrO_3$, with no trace of the starting materials.

Apparatus and procedure

A stacked-pellet assembly of the electrochemical cell, similar to that described elsewhere [19, 20], was used for the e.m.f. measurement. The reference electrode consisted of pure CaO mixed with pure CaF_2 in an equimolar ratio. The measuring electrode consisted of a mixture of ZrO_2, $CaZrO_3$ and CaF_2 in equimolar proportions. The mixtures were pelletized and sintered at 1200 K before assembling the cell. In preliminary experiments, the addition of CaF_2 to the oxide electrode constituents was found to be necessary for obtaining reproducible results. Minor variations in the mixing ratio of the constituents did not have any significant effect on the results obtained.

The reference and measuring electrodes were mounted on either side of the single-crystal CaF_2 electrolyte. A thin platinum mesh was inserted between the solid electrolyte and the electrode on each side. A platinum lead was spot-welded to each mesh. The pellets were pressed together with a system consisting of an alumina support tube, an alumina rod and springs [19, 20]. The assembly was housed inside an outer alumina tube, closed at both ends by brass fittings. The outer alumina tube was suspended inside a vertical resistance furnace such that the electrodes were maintained in the constant temperature zone. A foil of stainless steel was wrapped over the outer alumina tube surrounding the cell. The foil was grounded to minimize induced e.m.f. on the platinum leads from the furnace winding. The cell temperature was measured by a Pt/Pt–13%Rh thermocouple, calibrated against the melting point of gold. The thermocouple was placed adjacent to the measuring electrode. The temperature of the cell was controlled to ± 1 K.

The brass end caps attached to the outer alumina tube contain provisions for gas inlet and outlet, cell and thermocouple leads, and supports for springs. The alumina support tube and rod used for pressing the electrodes against the solid electrolyte were firmly fixed to the brass head. Pure oxygen was passed through the outer alumina tube at flow rates ranging from 2 to $10\ \mathrm{ml\ s^{-1}}$. The same gas stream flowed past each electrode. Because the equilibrium fluorine partial pressure over each electrode is extremely low, there is no danger of transport of fluorine from one electrode to the other via the gas phase.

The e.m.f. was measured by a high impedance ($>10^{12}\ \Omega$) digital voltmeter with a sensitivity of ± 0.1 mV. The reversibility of the e.m.f. was checked by microcoulometric titration in both directions. By passing a small direct current ($\approx 15\ \mu A$ for 200 s) through the cell using an external potential source, the chemical potential of fluorine at each electrode was altered by an infinitesimal amount. After passage of the current, the e.m.f. of the cell was monitored as a function of time. The reversibility of the cell was established when the e.m.f. returned to the same value after forward and reverse titrations at constant temperature. The reproducibility of the e.m.f. was also verified by making measurements during several cycles of increasing and decreasing temperature. The e.m.f. was also monitored as a function of the flow rate of the gas in the range 2–10 ml s^{-1}. To check for a possible temperature gradient across the cell, the e.m.f. of a symmetric cell with $CaO + CaF_2$ electrodes on either side of a single-crystal CaF_2 was measured as a function of temperature. The e.m.f. was found to be ± 0.2 mV without any systematic trends. X-ray diffraction analysis of the electrodes was performed after each experiment to check if there had been any change in their phase composition during the e.m.f. measurement. The composition of each phase in the electrode pellet was verified by energy-dispersive X-ray analysis (EDAX).

RESULTS AND DISCUSSION

The e.m.f. of cell I was independent of the flow rate of oxygen through the alumina tube enclosing the cell in the range 2–6 ml s^{-1}. At higher flow rates, there was a small effect on e.m.f., probably produced by differential cooling of the electrodes. Most experiments were carried out at a flow rate of 4 ml s^{-1}. The e.m.f. was reproducible on temperature cycling in the range 950–1226 K. The time required to attain constant e.m.f. varied from 12 to 90 ks, depending on the temperature of the cell, longer periods being required at lower temperatures. The low temperature limit of measurement was set by the sluggish response of the cell. Softening of single-crystal CaF_2 and the non-linear variation of the e.m.f. with temperature above 1220 K fixed the upper limit.

The temperature dependence of the reversible e.m.f. of the cell is shown in Fig. 1. The numbers and letters on the figure indicate the sequence of measurement. Within experimental error (± 0.3 mV), the e.m.f. is a linear function of temperature. The least-mean-squares regression analysis gives

$$E = 165.3 + 0.0694T(\pm 0.5) \text{ mV} \qquad (6)$$

The uncertainty limits correspond to twice the standard error estimate.

The X-ray diffraction analysis did not indicate any change in the phases present in the electrode pellets during high-temperature e.m.f. measurements. However, EDAX indicated a small solubility of CaO in the monoclinic form of ZrO_2. An attempt was made to measure the saturation solubility by equilibrating homogeneous mixture of ZrO_2 and $CaZrO_3$ in oxygen for approx. 120 ks at 1200 K and for approx. 600 ks at 900 K. The mixture, containing particles in the size range 20–40 μm, was pelletized before equilibration. However, EDAX analysis of different grains, using a beam size of 1 μm, did not give fully reproducible results. The maximum solubility of CaO in ZrO_2 evaluated from EDAX is approx. 3 mol% at 1200 K and approx. 2 mol% at 900 K. The compound $CaZrO_3$ was found to be stoichiometric.

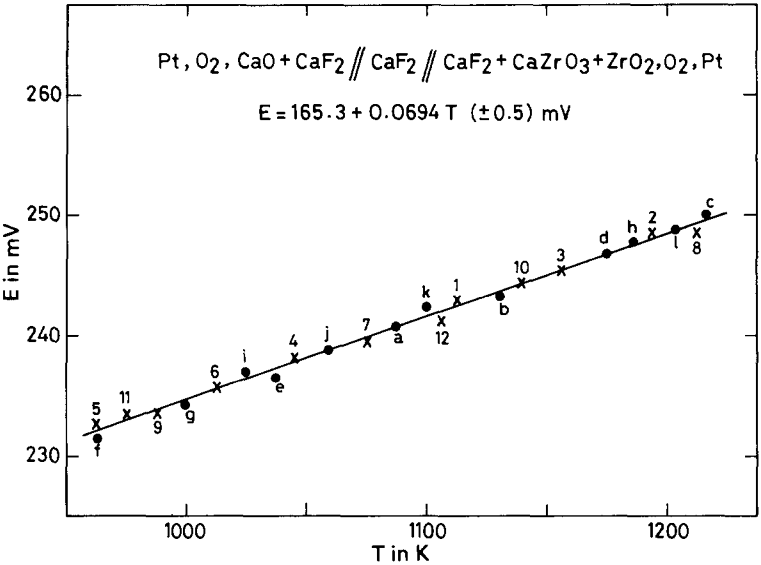

Fig. 1. Temperature dependence of the e.m.f. of cell I. Numbers and letters indicate the sequence of e.m.f. measurements.

The standard free energy of formation of $CaZrO_3$ according to reaction (3), calculated from the e.m.f. and the solubility of CaO in ZrO_2 using eqn. (4), can be expressed as

$$\Delta G_3^\ominus = -31\,590 - 13.9T(\pm 180)\ \mathrm{J\,mol^{-1}} \qquad (7)$$

The temperature-independent term in this equation represents the average value of the enthalpy charge for reaction (3) in the temperature range covered in the e.m.f. measurements. The "second-law" enthalpy of formation of $CaZrO_3$(o) from ZrO_2(m) and CaO(p) at a mean temperature of 1090 K is $-31.6 \pm 1.5\ \mathrm{kJ\,mol^{-1}}$. This is in excellent agreement with the high-temperature calorimetric value of $-31.3 \pm 4\ \mathrm{kJ\,mol^{-1}}$ reported by Muromachi and Navrotsky [10] at 1068 K. The enthalpy increment of $CaZrO_3$(o) above room temperature has been measured by three groups of researchers [11-13]. The average of these measurements in the temperature range 298-1300 K can be well represented by the simple equation

$$H_T^\ominus - H_{298.15}^\ominus = (122.8 \pm 1.9)[T - 298.15]\ \mathrm{J\,mol^{-1}} \qquad (8)$$

Combining this information with data for $H_T^\ominus - H_{298.15}^\ominus$ for ZrO_2(m) and CaO(p) given in the compilation of Pankratz [21], the standard enthalpy of formation of $CaZrO_3$(o) from component oxides at 298.15 K is obtained as $-32.6 \pm 4\ \mathrm{kJ\,mol^{-1}}$. This compares with values of $-30.5 \pm 4\ \mathrm{kJ\,mol^{-1}}$ reported by Lvova and Feodosev [7], $-31.4 \pm 4\ \mathrm{kJ\,mol^{-1}}$ by Korneev et al. [8], and $-40.8\ (\pm 0.5)\ \mathrm{kJ\,mol^{-1}}$ by Brown and Bennington [9] at 298.15 K. The average of the three bomb and acid-solution calorimetric measurements is -34.2 kJ mol^{-1} at 298.15 K, in good agreement with the value deduced in this study.

The temperature-dependent term in eqn. (7) represents the entropy charge for reaction (3) at 1090 K. Combining this with $S_T^\ominus - S_{298.15}^\ominus$ for the reactants and products, gives the standard entropy of $CaZrO_3$(o) at 298.15 K as 96.4 ± 3.5 J K^{-1} mol^{-1}. The standard entropies of ZrO_2 and CaO were taken from Pankratz [21]. The low-temperature heat capacity measurements on $CaZrO_3$ [11] suggest a value of 98.5 ± 2 J K^{-1} mol^{-1} for $S_{298}^\ominus$.

Pizzini and Morlotti [3] and Levitskii et al. [4] attempted to measure the activity of CaO in cubic zirconia solid solutions using the e.m.f. technique. The cubic phase prepared at very high temperature was used for e.m.f. studies at moderate temperatures using CaF_2 as the solid electrolyte. The composition and temperature ranges covered in these e.m.f. studies are superimposed on the phase diagram for the ZrO_2–CaO system in Fig. 2. Because the solubility of CaO in the monoclinic form of ZrO_2 has not been

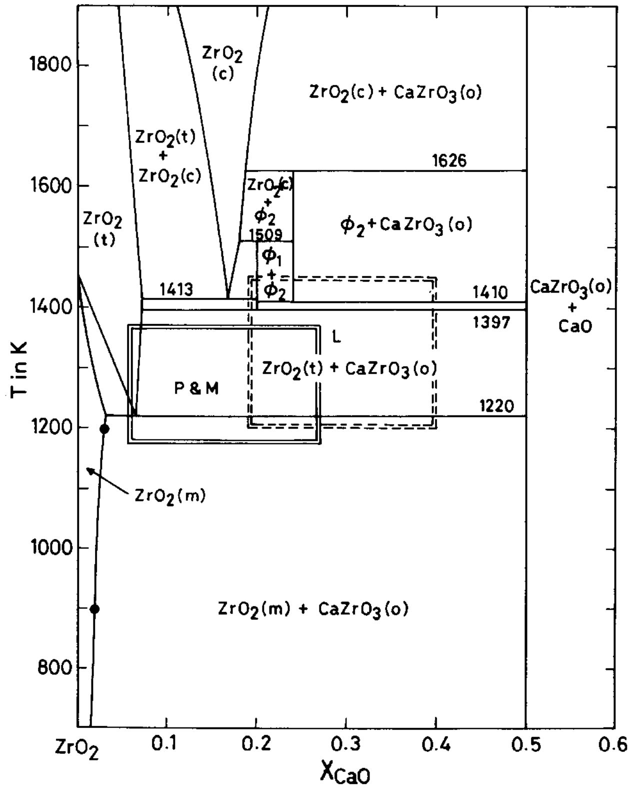

Fig. 2. Partial phase diagram for the system ZrO_2–CaO composed from data obtained in this study and in ref. 5. The composition–temperature range covered in the e.m.f. studies of Pizzini and Morlotti [3] (P&M) and Levitskii et al. [4] (L) are shown by rectangles superimposed on the phase diagram.

measured before, the approximate values obtained in this study are shown on the diagram. The domain of each e.m.f. study is represented by a rectangle. It is clear that the cubic phase is unstable under the experimental conditions employed. Furthermore, in view of the rather slow diffusion rates at the experimental temperatures, it is unlikely that equilibrium phases would have evolved in the course of their measurements. This conclusion is reinforced by the X-ray measurements of Pizzini and Morlotti [3], which indicate the presence of cubic phase only between 14 and 17 mol% CaO, again in contradiction to the phase diagram. The e.m.f. values reported by Pizzini and Morlotti [3] do not exhibit monotonic variation with composition at constant temperature. All the e.m.f. values lie in a band (± 10 mV) with an average value of 238 mV at 1200 K. This compares with the value of 248.6 ± 0.5 mV obtained in this study. The average value of the e.m.f. obtained by Levitskii et al. [4] is approx. 5 mV higher than that reported by Pizzini and Morlotti [3] and is closer to the result obtained in this study. Thus it may be concluded that the earlier e.m.f. studies [3, 4] correspond neither to metastable equilibrium representing the starting compositions used, nor to true equilibrium represented by the phase diagram. Therefore, only the results of this study provide true equilibrium values of the stability of $CaZrO_3$ at high temperatures; these are in good agreement with calorimetric information.

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