

Free Energy of Formation of BaThO₃ from E.M.F. Measurement

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The Gibbs free energy of formation of BaThO₃ from elemental oxides has been measured at temperatures between 853 and 903 K using a CaF₂ solid electrolyte galvanic cell. The galvanic cell consisted of Pt, O₂, CaO+CaF₂ || CaF₂ || BaThO₃+ThO₂+BaF₂, O₂, Pt EMF gave the standard Gibbs free energy for the reaction CaF₂+BaThO₃=CaO+BaF₂+ThO₂ as $\Delta G^\circ = 123111.031 - 117.597 T$ (J/mol).

Key words : BaThO₃, Gibbs free energy, E.M.F., Galvanic cell

I. Introduction

BaThO₃ is known to be an excellent proton conductor which is a potential candidate for the electrolyte of hydrogen concentrators and fuel cells. BaThO₃ is usually formed by the conventional ceramic processing method calcining the corresponding oxides, carbonates or nitrates, etc. at elevated temperatures ($\geq 1100^\circ\text{C}$).^{1,3)} The anticipated applicable temperature of this material is in the range of 500 to 1000°C. At these temperatures, the kinetics of solid-state processes are very sluggish due to the fact that the cation diffusion coefficients of most perovskites oxides are extremely small.¹⁾ Thus, regardless of the thermodynamic stability, these materials are generally expected to be kinetically stable at working temperatures. Even so, it would be of much value to know if this material is thermodynamically stable over the temperature range of interest. In this study, we determined the free energy of formation of BaThO₃ at high temperatures using galvanic cell method.

II. Materials

The reference electrode pellet was prepared by heating a compacted mixture of 80 wt% CaO and 20 wt% CaF₂ at 1273 K for 12 hr under dry oxygen atmosphere.⁴⁾ BaThO₃ was prepared by mixing ThO₂ and BaCO₃ in the stoichiometric proportion and heating in a furnace at 1673 K. BaThO₃ is known to have an orthorhombic structure and its x-ray diffraction data has also been reported by other researcher.⁵⁾ The working electrode was composed of an equimolar mixture of BaThO₃, ThO₂ and BaF₂ that had been heated in a furnace filled with dry oxygen at 973 K for 48 hr. Because the phase diagrams of the compounds for the working electrode are not available yet, each phase was examined by XRD after

heat treatment. CaF₂ powder was pressed and sintered under a highly dried argon atmosphere at 1373 K for 12 hr. During sintering, each ambient gas was passed through traps to obtain dry, CO₂-free gases. These traps were composed of P₂O₅, ascarite and H₂SO₄.

III. Experimental procedures

The solid electrolyte pellet of calcium fluoride was sandwiched between the reference and the working electrode of the cell. Each pellet was polished with sandpaper to improve electrical contact between them. Platinum wire was used to connect the platinum gauze to a high-impedance voltmeter. The whole cell assembly was placed inside a quartz tube as shown in Fig. 1. The temperature of the cell was monitored using a K-type (chromel/alumel) thermocouple which was positioned near the galvanic cell. The EMF of the cell was measured using a Keithley 617 digital electrometer of which the input-impedance is 10¹⁴ Ω. The most important thing in the operation of this cell was how to get rid of the CO₂ and H₂O impurity in the gas phase. Moisture reacts with

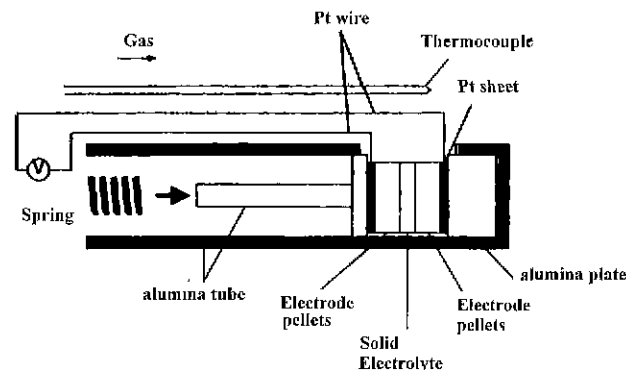


Fig. 1. Schematic diagram of galvanic cell.

the fluoride electrolyte to form the corresponding oxides on the surface of the cell. The reference electrode also reacts easily with CO₂ and H₂O in the gas phase, leading to unsteady EMF values. The reversible EMF values of the cell were measured in the temperature range of 853-903 K. The reproducibility of the EMF values was checked by a thermal cycle.

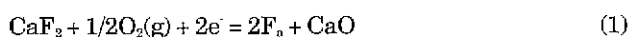
IV. Results and Discussion

Fig. 2. shows the EMF values of the galvanic cell vs. temperature (K). The EMF values of the cell maintains equilibrium for 7 days and dropped slowly. The cell construction is as follows.

O₂, Pt, CaO + CaF₂ || CaF₂ || BaThO₃ + ThO₂ + BaF₂, Pt, O₂

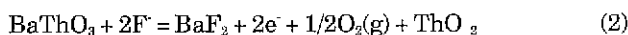
The half-cell reactions are as follows:

At left side (the reference electrode),



2F⁻ transport through the electrolyte(CaF₂) to the right side.

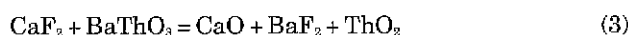
At right side (the working electrode),



Thus, the reference electrode becomes positive and the working electrode becomes negative provided the overall reaction is thermodynamically favorable. The value of EMFs vs. T(K) can be fitted to a linear equation

$$E = -0.3011 + 0.5795 \times 10^{-3} T(\text{V})$$

In terms of these EMF values, the Gibbs free energy of the reaction,



is given by the equation $\Delta G_{(3)}^\circ = -2EF = 58110.830 - 111.844T$ (J/mol) where *F* is the Faraday constant. The Gibbs free

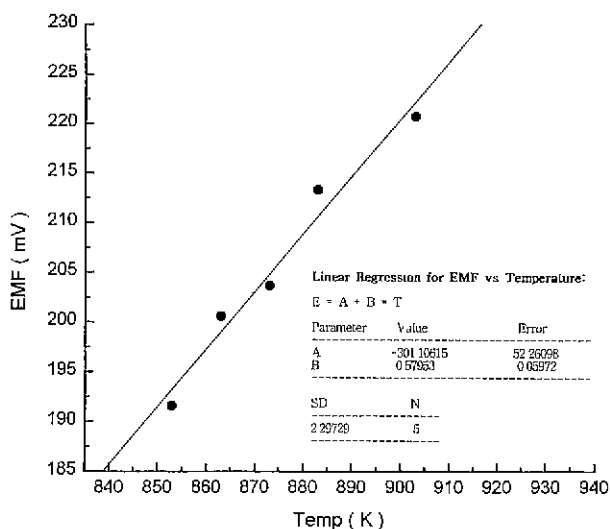


Fig. 2. Experimental EMF versus temperature.

energy change for the reaction,



can be obtained by using the data reported elsewhere⁹ as

$$\Delta G_{(4)}^\circ = 65000.2 - 5.75T \text{ (J/mol)}$$

From the reactions (3), (4) and the Gibbs free energy of the reaction (5)



is given by $\Delta G_{(5)}^\circ = \Delta G_{(3)}^\circ + \Delta G_{(4)}^\circ = 123111.031 - 117.597T$ (J/mol)

The equilibrium temperature for the coexistence of BaThO₃, BaO, ThO₂ is obtained when $\Delta G_{(5)}^\circ = 0$. This temperature is 1046 K or 773°C. Thus, BaThO₃ is stable with respect to the individual oxides at the temperature below ~773°C. Above this temperature, BaThO₃ is expected to decompose into BaO and ThO₂. There are no other thermodynamic data for the compound BaThO₃ against which the results of this study can be compared. The calorimetric studies of the formation of BaThO₃, or heat capacity measurement as a function of temperature, can confirm the results obtained in this study. Our data was cross-examined roughly by using another simple method, i.e. *in situ* high temperature-XRD analysis of the working electrode compounds in the range of room temperature to 800°C. Fig. 3. shows the XRD patterns of the working electrode. As is seen, the peak intensity of BaThO₃ decreased appreciably at 700~800°C(973~1073 K)

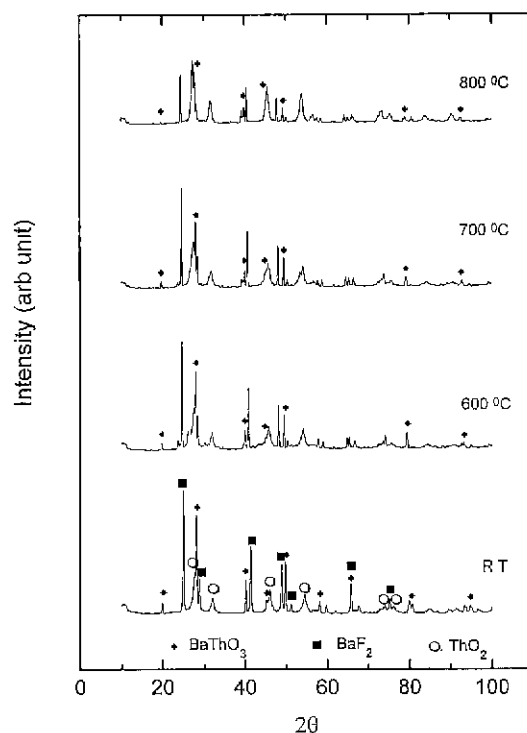


Fig. 3. XRD data of working electrodes at various temperatures.

compared to those at other temperatures and the peak intensity of the ThO₂ phase sharply increases. These results seem to support our experimental observation.

Acknowledgment

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