SYNTHESIS OF SrCeO₃, BaCeO₃, SrZrO₃ and BaZrO₃
AND THEIR REACTION WITH CO₂

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ABSTRACT

The log pCO₂ versus 1/T relationships of the equilibria
ACO₃ + ZrO₂ = AZrO₃ + CO₂,
ACO₃ + CeO₂ = ACeO₃ + CO₂ and
ACO₂ = AO + CO₂
in which A = Sr or Ba, were investigated. The methods which have been used are: thermodynamic equilibrium calculations, simultaneous thermogravimetry - differential thermal analysis, and high temperature X-ray diffraction.

In pure N₂ atmosphere the synthesis of the zirconates and cerates proceeds via
1) ACO₃ + AO + CO₂ and
2) AO + CeO₂ ↔ ACeO₃ or AO + ZrO₂ ↔ AZrO₃,

which is not calculated thermodynamically, but is apparently more favorable kinetically at low temperatures.

SrCeO₃ and BaCeO₃ react with 1 atm CO₂ below 1190°C and 1185°C, respectively. For mixtures with other gases, the decomposition temperatures can be estimated from the figures presented. SrZrO₃ and BaZrO₃ should react below 600°C and 550°C, respectively, but they are probably stable below these temperatures due to slow reaction rates.
1. INTRODUCTION

The advantage of the perovskite type oxides CaZrO$_3$, SrZrO$_3$ and BaZrO$_3$, compared to SrCeO$_3$ and BaCeO$_3$ for utilization in solid oxide fuel cells are their chemical stability and mechanical strength, as pointed out by Iwahara et al. (1).

We have investigated the following equilibria:

\[
\begin{align*}
\text{SrCO}_3 + \text{ZrO}_2 &= \text{SrZrO}_3 + \text{CO}_2 \\
\text{SrCO}_3 + \text{CeO}_2 &= \text{SrCeO}_3 + \text{CO}_2 \\
\text{SrCO}_3 &= \text{SrO} + \text{CO}_2 \\
\text{BaCO}_3 + \text{ZrO}_2 &= \text{BaZrO}_3 + \text{CO}_2 \\
\text{BaCO}_3 + \text{CeO}_2 &= \text{BaCeO}_3 + \text{CO}_2 \\
\text{BaCO}_3 &= \text{BaO} + \text{CO}_2
\end{align*}
\]  

(1) (2) (3) (4) (5) (6)

by using simultaneous thermogravimetry-differential thermal analysis (TG-DTA), in a pure CO$_2$ or N$_2$ flow, up to 1500°C, and high-temperature X-ray diffraction (HT-XRD) in pure 1 atm N$_2$ flow up to 900°C. The experimental results are compared with thermodynamic equilibrium calculations. Equilibria 2, 3, 5 and 6 have been studied before (2). These results will be referred to here only briefly.

2. EXPERIMENTAL ASPECTS

Samples

SrCO$_3$ (Merck 7861), BaCO$_3$ (Merck 1714: >99%), CeO$_2$ (Fluka 22390: >99%) and ZrO$_2$ (Fluka 96594: 99%) were used. The 50 mole% SrCO$_3$ or BaCO$_3$ - 50 mole% CeO$_2$ or ZrO$_2$ mixtures were made by dry mixing of the powders in an agate mortar.

TG-DTA

A Setaram TG-DTA 92 was used for simultaneous thermogravimetry and differential thermal analysis (TG-DTA) from ambient temperature up to 1500°C. A Pt-crucible was used, although it reacts with the BaCO$_3$ melt. It is assumed that the melting point or decomposition temperature of BaCO$_3$ is not influenced by this reaction. The heating rate was 20°C/min. A flow of CO$_2$ or N$_2$ was passed over the sample.
HT-XRD

For the high-temperature X-ray diffraction (HT-XRD) study an Enraf Nonius Guinier-Lenné camera was employed using Cu-Kα radiation. The powder samples, present on a Pt-grid, were heated with a rate of 600°C/h from ambient temperature up to 700°C, and with a rate of 10°C/h between 700 and 900°C in N₂ flow.

3. RESULTS AND DISCUSSION

Thermodynamic calculations

The thermodynamic data which were used were taken from Sorokina et al. (3) for SrCeO₃, from Leviskii et al. (4) for BaCeO₃, and from Barin (5) for all other compounds. The calculated log pCO₂ - 1/T relationships of the equilibria (1)-(6) are presented in figures 3 and 4 by solid lines.

Experiments

SrCO₃

An orthorhombic to rhombohedral phase transition takes place at 928°C (in 1 atm CO₂).

The decomposition of SrCO₃ at different CO₂ pressures has been measured before by Lander (6) and Baker (7).

In our TG-DTA experiments SrCO₃ starts to decompose to SrO at 1275°C in pure CO₂ at atmospheric pressure (see figure 1), which is slightly higher than the 1259°C found by Baker (7). These measured temperatures of decomposition are much higher than the calculated ones. The thermodynamic properties of SrCO₃ should be reinvestigated, which was also concluded by Busenberg et al. (8). We are now evaluating the thermodynamic properties of SrCO₃ and remeasuring the low temperature heat capacities by adiabatic calorimetry. The results of this study will be published elsewhere.

In N₂ flow, the HT-XRD data show the direct complete decomposition of SrCO₃ to SrO. The TG-DTA curve shows, however, two decomposition peaks. This 'two step' decomposition is probably due to the fact that the partial pressure of CO₂ increases during decomposition. The changes in the TG-DTA signals are gradual, indicating that kinetics play an important role.
BaCO₃

An orthorhombic to rhombohedral and a rhombohedral to cubic phase transition takes place at 817°C and 980°C, respectively (in 1 atm CO₂).

The decomposition of BaCO₃ at different CO₂ pressures has been measured before by Lander (6) and Baker (9).

In our TG-DTA experiments the BaCO₃ starts to melt and loose carbon dioxide at 1380°C in pure CO₂ at atmospheric pressure (see figure 2). This is in good agreement with the data of Baker (9). The melt attacks the Pt-crucible.

The measured temperatures of decomposition to BaO (6) at low pressures of CO₂ are in good agreement with the calculated ones.

In N₂ atmosphere the decomposition of BaCO₃ starts with the reaction to BaO, but after the CO₂ pressure has increased too much the decomposition proceeds to produce a melt which attacks the Pt-crucible, resulting in a very irregular DTA curve. The HT-XRD data demonstrate that BaCO₃ decomposes in N₂ to form solid BaO. The rhombohedral BaCO₃ which exists between 807°C and 971°C is not described in the JCPDS file.

50% SrCO₃ - 50% CeO₂ mixture

In pure CO₂ at atmospheric pressure the reaction proceeds as follows (see figure 1). First the reaction SrCO₃ + CeO₂ → SrCeO₃ + CO₂ takes place, starting at 1190°C, which is significantly higher than the calculated temperature (see figure 2). This discrepancy may be caused by incorrect thermodynamic data (see also SrCO₃). As this reaction is not completed at around 1275°C, decomposition of SrCO₃ takes place. From the 'two step' reverse reaction during cooling in CO₂, one can conclude that the reaction to SrCeO₃ did not go to completion during heating.

In pure N₂ at atmospheric pressure the HT-XRD data reveal that the reaction proceeds as follows:

SrCO₃ → SrO + CO₂
SrO + CeO₂ → SrCeO₃

which is not calculated thermodynamically, but is apparently kinetically more favourable at low temperatures.

50% BaCO₃ - 50% CeO₂ mixture

In pure CO₂ at atmospheric pressure the reaction of BaCO₃ + CeO₂ → BaCeO₃ + CO₂ starts at 1155°C (see figure 2), which is slightly higher than the calculated temperature (see figure 3). Subsequently the decomposition of BaCO₃ to BaO takes place. A hysteresis exists in the temperatures of thermal and gravimetric effects in the heating and cooling curve. This is probably due to the
formation of a melt.

In N₂ at atmospheric pressure the reaction proceeds analogous to the mechanism as described in the section 50% SrCO₃ - 50% CeO₂ mixture.

50% SrCO₃ - 50% ZrO₂ mixture

Thermodynamic equilibrium calculations reveal a temperature of 600°C for the equilibrium of SrCO₃ + ZrO₂ = SrZrO₃ + CO₂ at 1 bar CO₂. The true reaction temperature is probably slightly higher, because of incorrect thermodynamic data for SrCO₃. The TG-DTA data in pure CO₂ at atmospheric pressure (see figure 1) show a very gradual start of the reaction at 875°C. Also this reaction is not completed at around 1275°C, and hence decomposition of SrCO₃ takes place. The reverse reaction of SrO (which has not reacted to SrZrO₃) to SrCO₃ is observed during cooling. However, the reverse reaction of SrZrO₃ to SrCO₃ and ZrO₂ is not observed, indicating that this measured temperature of reaction is determined by kinetics and not by thermodynamics. This means that SrZrO₃ is stable in pure 1 atm CO₂ atmosphere, from room temperature up to 1500°C, although it should react below 600°C, according to thermodynamic calculations. This will be verified in the near future by TG-DTA experiment using a pure SrZrO₃ sample. This measured temperature of reaction has not been plotted in figure 3.

In N₂ at atmospheric pressure the HT-XRD data reveal that the reaction proceeds analogous to the mechanism as described in the section 50% SrCO₃ - 50% CeO₂ mixture.

50% BaCO₃ - 50% ZrO₂ mixture

Thermodynamic equilibrium calculations reveal a temperature of 550°C for the equilibrium of BaCO₃ + ZrO₂ = BaZrO₃ + CO₂ at 1 bar CO₂. The TG-DTA data in pure CO₂ at atmospheric pressure (see figure 2) show a very gradual start of the reaction at 975°C. This reaction is not completed at around 1380°C, and hence the decomposition of BaCO₃ to BaO takes place. During cooling no reverse reactions are observed. This probably means that BaZrO₃ is stable in pure 1 atm CO₂ atmosphere, from room temperature up to 1500°C, although this compound should react below 550°C, according to thermodynamic calculations. This will also be verified in the near future by TG-DTA experiment using a pure BaZrO₃ sample. This measured temperature of reaction has not been plotted in figure 4.
4. CONCLUSIONS

The synthesis of the zirconates and the cerates proceeds in pure N₂ atmosphere via
1) ACO₃ → AO + CO₂ and
2) AO + CeO₂ → ACeO₅ or AO + ZrO₂ → AZrO₃ (A is Sr or Ba),
which is not calculated thermodynamically. Apparently reaction 1 proceeds
kinetically more favourable at low temperatures.

SrCeO₄ and BaCeO₃ react with pure CO₂ below 1190°C and 1185°C,
respectively. For mixtures of CO₂ with other gases, the decomposition
temperatures can be estimated from figures 3 and 4. If one wants to apply these
cerates in solid oxide fuel cells, the operating temperatures should be high enough
and the partial pressure of CO₂ low enough to avoid the decomposition of the
cerate.

According the thermodynamic equilibrium calculations SrZrO₃ and
BaZrO₃ should react below 600°C and 550°C, respectively, but they are probably
stable below these temperatures due to slow reaction rates. This will be verified
in the near future by using pure zirconate samples.

The thermodynamic properties of SrCO₃, SrCeO₅ and BaCeO₃ need to be
reinvestigated.

The sintering of cerates

The decomposition of organic binders at low temperatures will produce
carbon dioxide, which will react with the cerate to form carbonate and ceria. The
volume of the product is larger than the volume of the starting material. The
calculated increase in volume at room temperature is about 35%. At higher
temperatures the carbonate will react back with ceria to cerate, causing a
decrease in volume. These changes in volume may be the cause of the low
relative density of sintered. To produce sintered of high relative density one should
therefore be able to
(1) avoid the use of binders by using powders of very small grain size or
(2) let the binders not decompose to carbon dioxide, by sintering in reducing
atmosphere.

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Figure 1. TG-DTA curves for SrCO$_3$, SrCO$_3$ + CeO$_2$ and SrCO$_3$ + ZrO$_2$ in CO$_2$ flow (1 atm). The mass% and $\Delta T$ data are presented in the upper and lower part of the figure, respectively.
Figure 2. TG-DTA curves for BaCO$_3$, BaCO$_3$ + CeO$_2$ and BaCO$_3$ + ZrO$_2$ in CO$_2$ flow (1 atm). The mass$\%$ and $\Delta$T data are presented in the upper and lower part of the figure, respectively.
Figure 3. Stability of SrO, SrCeO₃ and SrZrO₃ in CO₂ containing atmosphere.

Figure 4. Stability of BaO, BaCeO₃ and BaZrO₃ in CO₂ containing atmosphere.