Hydrothermal Synthesis of Carbonate-Free Strontium Zirconate: Thermodynamic Modeling and Experimental Verification

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A comprehensive thermodynamic model has been applied to predict the optimum conditions for the hydrothermal synthesis of phase-pure strontium zirconate. The model is based on the accurate knowledge of standard-state thermochemical properties of all species and a realistic activity coefficient model. The predictions are conveniently summarized in the form of phase stability and yield diagrams. Unlike our previous works, the diagrams are automatically generated using newly developed software, which makes it possible to analyze the effect of reactant identity and concentrations, contaminants, pH, and temperature as independent variables. The calculations revealed a high sensitivity of the synthesis to the identity of Sr precursors, Sr/Zr molar ratio of starting materials, and temperature as well as to the contamination with carbonates. The predictions have been confirmed experimentally at two temperatures (433 and 473 K) using strontium hydroxide or strontium nitrate as sources of Sr and a hydrazic zirconium dioxide as a source of Zr. Both the predictions and experiment demonstrate that phase-pure SrZrO3 can be obtained only when all starting materials are CO2-free.

Introduction

Recently, hydrothermal synthesis of perovskite-type ceramic materials has been extensively investigated using both theoretical and experimental techniques.1-6 It has been shown in our previous papers7-10 that accurate thermodynamic models can be constructed for a variety of hydrothermal systems of practical importance. These models make it possible to select effective, yet simple and inexpensive precursors and optimize process variables such as reagent concentrations, pH, temperature, and pressure. This methodology was applied to predict the optimum synthesis conditions for various perovskite-type7-10 materials. In all cases, the theoretical predictions were corroborated by experimental syntheses and efficient procedures were proposed for synthesizing phase-pure ceramic powders. In our previous studies,8-10 the thermodynamic predictions were summarized in the form of stability and yield diagrams that show the conditions where ceramic powders are stable and can be obtained with a desired phase purity. The diagrams were constructed manually in a painstaking way by repetitive chemical and phase equilibrium computations for a wide range of reaction conditions. In the present study, we will present the results of computations obtained via computer software that automatically generates these diagrams. This software is integrated with OLI Systems’ Environmental and Corrosion Simulation Programs.11

Our computations will focus on conditions favoring the synthesis of strontium zirconate. In contrast to the abundant literature on the synthesis of compounds such as BaTiO3 or PZT, relatively few researchers reported successful efforts to synthesize SrZrO3 in hydrothermal media. Galkin and Chukhlantsev12 outlined the synthesis of crystalline SrZrO3 powder at temperatures from 473 to 623 K using Sr(OH)2 and hydrous or anhydrous ZrO2 with a Sr/Zr ratio ranging from 1.5 to 3. To avoid carbonate contamination, the Sr(OH)2 was twice recrystallized and freed from carbonates and the synthesis was performed in CO2-free atmosphere. The powders were washed with hot water, apparently to remove the excess of solid Sr(OH)2, which is likely to form under these conditions. Kutty et al.13 also obtained pure SrZrO3 at 663 K using Sr(OH)2 and hydrothermally prepared ultrafine ZrO2 (monoclinic) powder.

In this paper, we first apply our electrolyte solution model to compute the thermodynamic equilibrium states
in the Sr–Zr–H2O system and its Zr–H2O subsystem. Then, we use the results of the computations to construct stability and yield diagrams, which serve as tools to determine the optimum synthesis conditions of phase-pure SrZrO3. The predictions are specifically designed to take into account the effect of contamination with CO2. Finally, we use the predictions to define the range of conditions for obtaining phase-pure SrZrO3. These conditions are further verified in a series of experiments.

Theoretical Predictions

The theoretical model for rigorous simulation of thermodynamic equilibrium in heterogeneous, solid–liquid hydrothermal systems has been described in detail in a previous paper.7 To apply the model to a particular system, it is necessary to enumerate all solid, aqueous, and vapor species that may be important in the system. For these species, it is further required to specify the standard-state thermochemical properties, i.e., the standard Gibbs energies ΔG°, enthalpies ΔH° of formation, and entropies S° at a reference temperature (298.15 K) as well as partial molar volumes V° and heat capacities C° as functions of temperature.

The thermochemical data14–19 for the species in the Sr–Zr–CO2–H2O system that have not been presented earlier9, 10 are listed in Table 1. The model utilizes these data in conjunction with a comprehensive activity coefficient model21 to calculate the equilibrium concentrations of all species in all phases. Repetitive application of the model for different input concentrations of Sr and Zr precursors as well as pH-adjusting agents (mineralizers) makes it possible to construct stability and yield diagrams, that show the reaction conditions for which a given product is stable and can be synthesized with an assumed yield.8–10 In this work, computer software has been developed for the automatic generation of these diagrams.

As the y-axis variable of both stability and yield diagrams, the program uses the input concentrations of one or more starting materials. The ratios of the concentrations can be held constant at a predetermined value. For example, the input concentrations of Sr(OH)2 and ZrO2 can be varied along the y-axis with their ratio kept constant at 1.0. As the x-axis variable, the program can use either pH or the input concentration of a pH-adjusting agent. If pH is chosen as the x-axis variable, the program changes the pH by adding varying amounts of a selected acid (such as HNO3 or HCl) and can be synthesized with an assumed yield.8–10

![Table 1. Standard-State Properties of Individual Species in the Sr–Zr–CO2 Hydrothermal System](image)

<table>
<thead>
<tr>
<th>Aqueous Species</th>
<th>Zr4+</th>
<th>ZrOH3+</th>
<th>Zr(OH)2+</th>
<th>Zr(OH)3+</th>
<th>Zr(OH)4+</th>
<th>Zr(OH)6+</th>
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<tr>
<td>ΔG° (kJ·mol⁻¹)</td>
<td>-557.60</td>
<td>-769.63</td>
<td>-1022.1</td>
<td>-1240.1</td>
<td>-1652.2</td>
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<td>ΔH° (kJ·mol⁻¹)</td>
<td>-628.98</td>
<td>-889.1</td>
<td>-1140.6</td>
<td>-1395.8</td>
<td>-1966.2</td>
<td>-1675.4</td>
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<tr>
<td>S° (J·mol⁻¹·K⁻¹)</td>
<td>-461.5</td>
<td>-299.6</td>
<td>-753.5</td>
<td>-45.95</td>
<td>-109.9</td>
<td>-42.94</td>
</tr>
<tr>
<td>C° (mol·l⁻¹·K⁻¹)</td>
<td>12.97</td>
<td>185.8</td>
<td>75.72</td>
<td>389.9</td>
<td>619.5</td>
<td>382.8</td>
</tr>
<tr>
<td>V°10⁶ (m³·mol⁻¹)</td>
<td>-54.3</td>
<td>-12.70</td>
<td>14.46</td>
<td>22.86</td>
<td>34.53</td>
<td>36.92</td>
</tr>
</tbody>
</table>

| Carbonate-Free Strontium Zirconate Chem. Mater., Vol. 9, No. 5, 1997 1117 |
|----------------|------|--------|----------|----------|----------|----------|
| Aqueous Species | Zr°(OH)4⁺ | Zr°(OH)5⁻ | Zr°(OH)6⁺ |
| ΔG° (kJ·mol⁻¹)  | -625.0 | -2837.6 | -4093.7 |
| ΔH° (kJ·mol⁻¹)  | -2958.0 | -3195.3 | -4518.1 |
| S° (J·mol⁻¹·K⁻¹) | -850.9 | -700.8 | -745.4 |
| C° (mol·l⁻¹·K⁻¹) | 491.5 | 964.0 | 1812.9 |
| V°10⁶ (m³·mol⁻¹) | -33.77 | -10.89 | 43.0 |
| ref             | 15    | 15      | 15       |

<table>
<thead>
<tr>
<th>Solid Species</th>
<th>SrZrO3</th>
<th>ZrO2</th>
<th>ZrCl4</th>
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</thead>
<tbody>
<tr>
<td>ΔG° (kJ·mol⁻¹)</td>
<td>-1681.7</td>
<td>-1039.7</td>
<td>-889.27</td>
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<tr>
<td>ΔH° (kJ·mol⁻¹)</td>
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<td>-1097.5</td>
<td>-979.81</td>
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<tr>
<td>S° (J·mol⁻¹·K⁻¹)</td>
<td>115.10</td>
<td>50.359</td>
<td>181.418</td>
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<tr>
<td>C° (mol·l⁻¹·K⁻¹)</td>
<td>103.39</td>
<td>56.053</td>
<td>119.77</td>
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<td>a (mol·l⁻¹·K⁻¹)</td>
<td>124.064</td>
<td>69.547</td>
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<tr>
<td>b (mol·l⁻¹·K⁻¹)</td>
<td>7.263</td>
<td>14.245</td>
<td></td>
</tr>
<tr>
<td>c (mol·l⁻¹·K⁻¹)</td>
<td>-2.16156</td>
<td>-14.00</td>
<td>-8.36582</td>
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<tr>
<td>V°10⁶ (m³·mol⁻¹)</td>
<td>41.55</td>
<td>21.15</td>
<td>83.14</td>
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<tr>
<td>ref</td>
<td>14, 19</td>
<td>14, 18</td>
<td>14, 19</td>
</tr>
</tbody>
</table>

a Heat capacities are calculated from the relation C° = a + bT + cT⁻².

15 Shock, E., private communication.
ZrO$_2$ in water using the ideal solution approximation

The symbols ZRO$_2$PPT, ZRION, ZROH$_{10}$ION, ZROH$_{2}ION$, ZROH$_{3}ION$, and ZROH$_{5}ION$ denote ZrO$_2$(s), Zr$^{4+}$, ZrOH$^{3+}$, Zr(OH)$_2^{2+}$, Zr(OH)$_3^{+}$, and Zr(OH)$_5^{-}$, respectively.

Figure 1. Calculated phase stability and yield diagram for the Zr hydrothermal system at 298 K. The symbols ZRO$_2$PPT, ZRION, ZROH$_{10}$ION, ZROH$_{2}ION$, ZROH$_{3}ION$, and ZROH$_{5}ION$ denote ZrO$_2$(s), Zr$^{4+}$, ZrOH$^{3+}$, Zr(OH)$_2^{2+}$, Zr(OH)$_3^{+}$, and Zr(OH)$_5^{-}$, respectively.

The stability diagrams include two types of lines: the solid lines denote the states of incipient precipitation of solids whereas the dotted lines show the loci where the desired yield of the product.

The yield areas are shown in the diagrams as shaded fields.

**Zr–H$_2$O System.** First, it is worthwhile to investigate the phase behavior of the system Zr–H$_2$O in order to understand the properties of zirconium precursors, which are used for the synthesis of SrZrO$_3$. Adair et al. have previously calculated a stability diagram for ZrO$_2$ in water using the ideal solution approximation (i.e., with all activity coefficients set equal to one). In our work, however, we utilize a realistic model for solution nonideality. Figures 1 and 2 show combined stability and yield diagrams for the Zr–H$_2$O system at 298 and 433 K, respectively, as a function of pH of the solution and input molalities of zirconium species (m$_{ZrO_2}$). At low concentrations of Zr, the vertical lines separate the stability fields of Zr$^{4+}$, ZrOH$^{3+}$, Zr(OH)$_2^{2+}$, Zr(OH)$_3^{+}$, and Zr(OH)$_5^{-}$. Although polynuclear zirconium species are present in the system (cf. Table 1), they are always much less abundant than the species shown in Figures 1 and 2. The incipient precipitation line for ZrO$_2$ has a parabolic shape and shows a minimum at about pH 5.5. In the acidic (low pH) region of the diagram, the incipient precipitation line slightly depends on the chemical identity of the acid that is used to adjust the solution pH. The solid line in Figure 1 was obtained with nitric acid. If HCl was used instead of HNO$_3$, the incipient precipitation line in strongly acidic solutions would be somewhat shifted toward higher pH because HCl more easily solubilizes zirconia in the form of chloride complexes such as ZrCl$_3^{+}$ and ZrCl$_2^{2+}$.

The shaded areas show the loci where ZrO$_2$ will precipitate from the solution with a yield of more than 99.9%. It is worth noting that the region of 99.9% yield of ZrO$_2$ is very large and covers a wide pH range (e.g., from pH = 1.0 to pH = 14 at m$_{ZrO_2} = 1.0$). However, ZrO$_2$ can be solubilized in both very acidic and very alkaline environments. The stability of solid ZrO$_2$ is relatively weakly affected by temperature. As shown in Figure 2, the stability of ZrO$_2$ in a very acidic solution is somewhat higher at 433 K than at 298 K. For alkaline solutions, the temperature effect is very small. In such solutions, ZrO$_2$ dissolves and Zr(OH)$_2^{2+}$ becomes the dominant species for both temperatures. Our predictions are qualitatively similar to those obtained from an ideal-solution stability diagram. Significant differences (by about 1 pH unit) are noted only for more concentrated solutions (i.e., above 0.01 M), especially in the strongly acidic and alkaline range.

**Sr–Zr–H$_2$O System.** For the calculation of the stability and yield diagrams for SrZrO$_3$, we used ZrO$_2$ (monoclinic) as a source of Zr and strontium nitrate or hydroxide as source of Sr. Figures 3 and 4 show the calculated stability and yield diagrams for the Sr–Zr hydrothermal system at 433 and 473 K, respectively. The input concentrations of Sr(NO$_3$)$_2$ and ZrO$_2$ are used as independent variables with their ratio fixed at 1.0. In the homogeneous aqueous region, the dominant Sr species are Sr$^{2+}$, SrOH$^{+}$, Sr(NO$_3$)$_2$(aq) and SrNO$_3^{3+}$. The
nitrate complexes result from the presence of NO$_3^-$ ions in Sr(NO$_3$)$_2$ as well as from the addition of nitric acid to vary pH. The stability of the Sr(NO$_3$)$_2$(aq) and Sr(NO$_3$)$_2^{+}$ complexes in the aqueous phase may somewhat affect the yield diagram because it favors the presence of Sr species in solution and not in the solid phase. The precipitation of SrZrO$_3$ begins at pH values starting from 10.4 at 433 K and from 9.6 at 473 K when the input concentration of precursors is 1 m. These values increase as the solution becomes more dilute with respect to Sr and Zr. An increase of temperature by 40 K shifts the line downward by about 0.8–1 pH units depending on molality.

Figures 3 and 4 also show the calculated yield of SrZrO$_3$ as a function of pH and input molality of starting materials at 433 and 473 K, respectively. The region of nearly complete yield (above 99%) of strontium zirconate is very small and is much smaller than the stability region. The size of the complete yield region is somewhat influenced by the chemical identity of the

Sr precursor and temperature. This is illustrated in Figure 5, which shows the stability and yield diagram at 473 K when Sr(NO$_3$)$_2$ is replaced by Sr(OH)$_2$ as a source of Sr. The Sr precursor effects can be explained by specific interactions between ions in the solution, which affect the activity coefficients. In particular, we are dealing with the preferential formation of Sr(NO$_3$)$_2^+$ and Sr(NO$_3$)$_2$(aq) at high molalities (m$_{Sr(NO_3)_2}$ > 0.1), which shifts the equilibrium toward dissolved aqueous Sr species and away from the precipitation of SrZrO$_3$. The nearly complete yield field somewhat widens with temperature (cf. Figures 3 and 4) in analogy to the stability field.

The stability and yield diagrams with pH as an independent variable (i.e., Figures 3–5) do not indicate how much of a pH-adjusting agent is necessary to synthesize the desired product. Therefore, we construct diagrams in which the Sr and Zr precursors, with a fixed molar ratio, are retained as y-axis variables and pH is replaced with the molality of a base (e.g., KOH) as an x-axis variable. Figures 6 and 7 show such diagrams at 473 K when Sr(NO$_3$)$_2$ and Sr(OH)$_2$ are used as Sr

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**Figure 3.** Calculated phase stability and yield diagram for the Sr–Zr hydrothermal system at 433 K for Sr/Zr = 1.0 using Sr(NO$_3$)$_2$ as a source of strontium. The symbols SRNO32AQ, SRNO3ION, SIRON, SROHION, and SRRZRO3PPT denote Sr(NO$_3$)$_2$(aq), SrNO$_3$$^{+}$, Sr$^{2+}$, and SrOH$^+$, respectively.

**Figure 4.** Calculated phase stability and yield diagram for the Sr–Zr hydrothermal system at 473 K for Sr/Zr = 1.0 using Sr(NO$_3$)$_2$ as a source of strontium.

**Figure 5.** Calculated phase stability and yield diagram for the Sr–Zr hydrothermal system at 473 K for Sr/Zr = 1 using Sr(OH)$_2$ as a source of strontium.

**Figure 6.** Calculated phase stability and yield diagram as a function of the input amount of KOH at 473 K for Sr/Zr = 1 using Sr(NO$_3$)$_2$ as a source of strontium.
sources, respectively. Figure 6 shows that a substantial molality of KOH is always necessary to precipitate phase-pure SrZrO₃ ($m_{KOH} > 1.6$). The necessary amount of KOH reaches a minimum when the amount of both Sr(NO₃)₂ and ZrO₂ is 0.22 m. It increases for both lower and higher input concentrations of starting materials. For practical purposes, an amount of KOH greater than 3 m is recommended. At lower temperatures, such as 433 K, the necessary amount of KOH increases to 4.5 m with a reduction in the area of the 99% yield region. If Sr(OH)₂ is used, the amount of KOH becomes much smaller but cannot be completely eliminated (see Figure 7). In this case, the minimum amount of KOH is as low as 0.2 m when the input concentration of Sr(OH)₂ is 1 m but rises to 1.6 m for an input concentration of 0.1 m.

Since the nearly complete yield region of SrZrO₃ is relatively small and limited to high pH and input molalities of Sr(NO₃)₂ and Sr(OH)₂, it was of interest to examine the influence of an excess amount of Sr precursor on the stability and yield. The excess amount of Sr may be introduced using Sr(NO₃)₂ or Sr(OH)₂ as starting materials. First, we consider Sr(NO₃)₂. Figure 8 shows the calculated yield diagram of SrZrO₃ at 473 K for the Sr/Zr ratio equal to 1.1. In this case, SrZrO₃ will be the first solid phase to precipitate from the solution as shown by the longer solid line in Figure 8. Within the nearly complete yield region of SrZrO₃ (shaded area), the excess amount of Sr precipitates as Sr(OH)₂. The precipitation of Sr(OH)₂ starts at the solid line that intersects the shaded area in Figure 8. At still higher pH values, more than 99% of the excess amount of Sr will precipitate as Sr(OH)₂. This is due to the fact that the solubility of Sr(OH)₂ is sufficiently low for the nearly complete precipitation of the excess amount of Sr in very strongly alkaline solutions.

It is worthwhile to note that the excess of Sr in the solution shifts the equilibrium so that pure SrZrO₃ precipitates at lower pH values (cf. Figure 8, Sr/Zr = 1.1) and reduces the amount of the mineralizer. This is illustrated in Figure 9 on a plot versus the molality of KOH. Comparison of Figures 6 and 9 reveals that the nearly complete yield region is significantly enlarged by the excess amount of Sr. Consequently, a smaller amount of KOH is needed for the synthesis (i.e., 0.50 m solution of KOH as opposed to 2.05 m for $m_{ZrO₂} = 0.1$).

![Figure 7](image7.png)  
**Figure 7.** Calculated phase stability and yield diagram as a function of the input amount of KOH at 473 K for Sr/Zr = 1 using Sr(OH)₂ as a source of strontium.

![Figure 8](image8.png)  
**Figure 8.** Calculated phase stability and yield diagram at 473 K for Sr/Zr = 1.1 using Sr(NO₃)₂ as a source of strontium.

![Figure 9](image9.png)  
**Figure 9.** Calculated phase stability and yield diagram as a function of the input amount of KOH at 473 K for Sr/Zr = 1.1 using Sr(NO₃)₂ as a source of strontium.

For all Sr/Zr ratios greater than 1.0, the pH interval in which we can obtain pure SrZrO₃ (not contaminated by Sr(OH)₂) is limited and has a similar shape which is illustrated in Figures 9 and 10. In other words, an excess of Sr shifts both the 99% yield region and the beginning of precipitation of Sr(OH)₂ toward lower pH values. Thus, an excess of Sr is useful provided that the synthesis is performed in the pH region where Sr(OH)₂ does not precipitate. This point is illustrated in detail in Table 2, which shows the minimum and maximum amounts of KOH, for which phase-pure
SrZrO$_3$ is obtained with 99% yield without the precipitation of Sr(OH)$_2$. As shown in Table 2, this “window” of KOH amounts strongly depends on the Sr/Zr precursor ratio and shifts to lower KOH amounts as the Sr/Zr ratio increases. The window becomes quite narrow when the initial concentration of starting materials is high (e.g., $m_{ZrO_2} > 1.0$).

Figure 11 shows the yield diagram for the Sr–Zr hydrothermal system at 473 K using Sr(OH)$_2$ as a starting material. The Sr/Zr ratio is equal to 2.0. The beginning of precipitation of SrZrO$_3$ remains almost the same as in the case of Sr(NO$_3$)$_2$ (cf. Figure 10). The region of nearly complete yield of SrZrO$_3$ is much greater than for Sr/Zr = 1.0 and starts at lower amounts of KOH (cf. Figure 7) and correspondingly lower pH values (cf. Figure 5). Therefore, no mineralizer is necessary when the input concentration of Zr exceeds 0.02 M. The nearly complete yield fields in Figures 10 and 11 are similar except for the concentrated solutions ($m_{ZrO_2} > 0.01$) where the formation of complexes between Sr$^{2+}$ and NO$_3^-$ causes a difference.

As evident from the diagrams, an excess of Sr is very useful because it makes it possible to reduce the use of the mineralizer (for Sr(NO$_3$)$_2$ and Sr(OH)$_2$) or eliminate it altogether (for Sr(OH)$_2$). Subsequently, the probability of inclusion of extraneous cations (i.e., K$^+$) into the crystal lattice is reduced. For our working conditions ($m_{ZrO_2} = 0.1$), it is possible to calculate the range of Sr/Zr molar ratio for which no mineralizer is necessary and no Sr(OH)$_2$ precipitates. Our calculations show that at 433 K this should be between 1.8 and 4.4, and for 473 K it should be between 1.2 and 2.6.

**Effect of CO$_2$ Contamination.** As described in the previous section, the synthesis of phase-pure SrZrO$_3$ is thermodynamically feasible when ZrO$_2$ is used with (1) Sr(NO$_3$)$_2$ and KOH for $Sr/Zr > 1.0$, where the amount of KOH is in the intervals shown in Table 2; (2) Sr(OH)$_2$ for $1.8 < Sr/Zr < 4.4$ at 433 K and $1.2 < Sr/Zr < 2.6$ at 473 K for $m_{ZrO_2} = 0.1$ and without KOH.

There are many ways to introduce CO$_2$ into the Sr–Zr–H$_2$O system. Here, we classify them and assess their importance. We may introduce CO$_2$ (1) with starting materials (i.e., with Sr(OH)$_2$, KOH, and hydroxrous ZrO$_2$); (2) during the preparation of the precursor solution by the absorption of CO$_2$ from air; (3) after the synthesis (i.e., during washing, filtration, etc.).

To eliminate the risk of carbonate contamination with starting materials, all reagents should be free from carbonates. However, carbonate-free Sr(OH)$_2$, Sr(OH)$_2$·8H$_2$O, and KOH are not available commercially. Commercially available alkaline-earth hydrates usually contain 0.5–3 wt % of CO$_2$. If all carbonate from this precursor was incorporated into the SrZrO$_3$ product, it may lead to a CO$_2$ content of 0.60–3.4 wt % in SrZrO$_3$. The 99.99% (adjusted to cation) electronic grade KOH contains 0.4 wt % of K$_2$CO$_3$ according to the manufacturer (Aldrich). Assuming that all K$_2$CO$_3$ contained in KOH converts to SrCO$_3$, the weight percent of SrCO$_3$ in the final product can be calculated. We can expect that using the Sr/Zr ratio greater than 1.0 would reduce the amount of SrCO$_3$ in our product. Our calculations show that for the Sr/Zr ratio equal to 1.0 and 2.0, SrZrO$_3$ will contain 2.1 and 0.32 wt % of SrCO$_3$, respectively.

At the same time, we can expect that the hydrolysis of zirconium isopropoxidewhich is used as a precursor in the presence of atmospheric CO$_2$ is accompanied by the formation of nonstoichiometric amorphous basic zirconium carbonate.$^{25,26}$ This phenomenon takes place at pH values between 3.9 and 8.5–9.0. It is reasonable to assume that the formation of hydrous ZrO$_2$ takes place within this pH range in our study.

The problem of contamination of the solution with carbonates during preparation of starting materials has been discussed in our previous paper.$^{10}$ It was shown that the contact of alkaline strontium precursors with an open CO$_2$-containing air atmosphere will lead to a contamination with SrCO$_3$ when the input concentration of Sr is greater than about $10^{-4}$ m. Thus, it is beneficial to avoid the contact with atmosphere during the preparation of reagents and after the synthesis. However, the absorption of atmospheric CO$_2$ may require a substantial amount of time which could be much longer than the time required for experimental manipulations. Washing and vacuum filtering of the synthesis products in air may cause additional contamination, especially when an excess amount of strontium is present in alkaline environments. However, the existing carbonate content of starting materials appears to be the major determinant of the purity of the product. The relative importance of the sources of contamination of SrZrO$_3$ with SrCO$_3$ will be further identified in this study.

For further simulations, we assume that the CO$_2$ contamination results primarily from the CO$_2$ content of starting materials. Therefore, we have constructed stability diagrams in which the amount of CO$_2$ is varied proportionally to the amount of the Sr and Zr precursors. This simulates a real-world situation in which CO$_2$ is a fixed fraction of a reactant. Figure 12 shows the effect of CO$_2$ on the stability and yield diagram plotted against the pH when the input amount of CO$_2$ is equal to 0.085 times the amount of ZrO$_2$. This amount corresponds to the average content of carbonate in hydrous ZrO$_2$ and KOH in our reactions. Despite the small CO$_2$ content of the system, SrCO$_3$ is present in alkaline environments. However, the existing carbonate content of starting materials appears to be the major determinant of the purity of the product.
verystableanditsstabilityrangealmostoverlapswith
the nearly complete yield range of SrZrO3. SrZrO3 is
predicted to be carbonate-free only in dilute solutions
at high pH values. Figure 13 shows an analogous
diagram calculated with the input molality of KOH as
an independent variable. In this case, the input amount
of CO2 is approximately 16 times lower than that in
Figure 12. Despite the lower CO2 content, SrCO3
remains stable and contaminates the product. The
incipient precipitation line of SrCO3 runs from the input
molality of ZrO2 equal to 0.001–0.005 m depending on
the KOH input. Above this line, practically all CO2
converts into SrCO3 and precipitates. Thus, SrZrO3
would be also contaminated with SrCO3. For all practi-
cal purposes, CO2 will always quantitatively precipitate
in the 99% yield region of SrZrO3 and contaminates the
product even when the amount of CO2 is very low. The
carbonate contamination is practically independent of
temperature. Moreover, the SrCO3 does not signifi-
cantly influence the stability and yield of SrZrO3. Very
similar behavior is observed when Sr(OH)2 is used as
source of Sr. This is illustrated in Figure 14 at T =
473 K.

**Experimental Approach**

To verify the theoretical predictions, experimental syntheses
were performed using Sr(NO3)2 or Sr(OH)2·8H2O as sources
of Sr and hydrous ZrO2 as a source of Zr. The initial
concentration of 0.1 m was chosen for ZrO2 and KOH was used
as a pH-adjusting agent. The Sr/Zr ratios ranging from 1.0
to 3.0 were used. Syntheses were performed at 433 and 473
K in the three regions of the stability and yield diagrams that
were determined from the calculations, i.e., (1) Region of
complete instability of SrZrO3 (zero yield, outside the stability
field of SrZrO3). (2) Region of incomplete reaction (between
the incipient precipitation line and nearly complete yield area).
In both regions (1) and (2), reactions were performed for Sr/

| mZrO2 | T = 433 K | T = 473 K |
|-------|--|---|---|
| m[OH] (min) | mKOH (max) | m[OH] (min) | mKOH (max) |
| Sr/Zr 1.0 | 0.1 | 1.05 | 1.1 | 2.0 | 5.0 | 1.0 | 1.05 | 1.1 | 2.0 | 5.0 |
| mZrO2 = 1.0 | 0.1 | 1.05 | 1.1 | 2.0 | 5.0 | 1.0 | 1.05 | 1.1 | 2.0 | 5.0 |

**Figure 11.** Calculated phase stability and yield diagram as
a function of the input amount of KOH at 473 K for Sr/Zr =
2.0 using Sr(OH)2 as a source of strontium. The solid circle
denotes experimental conditions for which phase-pure SrZrO3
was obtained.

**Figure 12.** Calculated phase stability and yield diagram at
473 K for Sr/Zr = 1.1 using Sr(NO3)2 as a source of strontium
when the amount of CO2 in the starting materials is equal to
0.085 times the amount of ZrO2. The symbols denote experi-
mental conditions for which the following products were
obtained: (×) ZrO2, (+) SrCO3 + ZrO2, (○) SrZrO3 + ZrO2 +
SrCO3, (●) SrZrO3 + SrCO3.

**Figure 13.** Calculated phase stability and yield diagram at
473 K for Sr/Zr = 2.0 using Sr(NO3)2 as a source of strontium
when the amount of CO2 in the starting materials (i.e., KOH)
is equal to 0.0054 times the amount of ZrO2. The solid circle
denotes experimental conditions for which SrZrO3 contami-
nated with 0.37 wt % of SrCO3 was obtained.
Standards (JCPDS). The morphology of the particles was obtained powders. Finally, Fourier transform infrared (FTIR) analysis was used to detect species derived from carbon dioxide exposure. Spectra were compiled from 70 scans measured between 4000 and 400 cm$^{-1}$ with 4 cm$^{-1}$ resolution.

Reagents and Procedures. As reagents, Sr(NO$_3$)$_2$ (Fisher Scientific, Fair Lawn, NJ, >99.9%), Sr(OH)$_2$·8H$_2$O (Johnson Matthey, Alfa Aesar, Ward Hill, MA, >99.9 wt % on metal basis) were used. In our previous paper, we found that crystalline ZrO$_2$ was not sufficiently reactive to react quantitatively with the aqueous reagents. The hydrous zirconia is an amorphous, nanostructured, high-surface-area powder. Its reactivity is due to the large surface area. According to BET measurements, the specific area of hydrous ZrO$_2$ is 272 m$^2$/g, whereas that of crystalline ZrO$_2$ is 4.9 and 18.3 m$^2$/g for the commercial powders of Fisher and Tosoh (Shou-ku, Tokyo, Japan), respectively. Therefore, we used freshly precipitated hydrous ZrO$_2$ as described in our previous paper. To adjust pH, KOH (Aldrich, Chemical Co., Milwaukee, WI, semiconductor grade, 99.9% wt % on metal basis) was used. For the reactions that were performed in an inert gas (Ar) atmosphere, a glovebox (VAC Vacuum Atmosphere Co., Model DLX-001-S-P, Hawthorne, CA) was used. The amount of CO$_2$ in freshly precipitated hydrous ZrO$_2$ was estimated using the wet chemical method$^{27}$ described earlier. Our ZrO$_2$ powders contain about 1.3 wt % of CO$_2$. The small content of CO$_2$ in hydrous ZrO$_2$ precludes its detection by TGA analysis which shows a smooth gradual weight loss of about 32–34 wt % to 700 K. Beyond 700 K, no further weight loss is observed. This is due to the evolution of water, organic residuals and CO$_2$. Also, we checked Sr(OH)$_2$·8H$_2$O for CO$_2$ content using the same wet chemical method. It was revealed that Sr(OH)$_2$·8H$_2$O contained approximately 1.0 wt % of CO$_2$. This prompted us to purify this reactant. For this purpose, we removed SrCO$_3$ by filtering SrCO$_3$ contaminations from a hot stock solution of Sr(OH)$_2$·8H$_2$O. The obtained stock solution has been used for the reactions within the region of nearly complete yield of SrZrO$_3$. Commercial KOH contained 0.4 wt % of K$_2$CO$_3$ according to our wet chemical analysis, which was in agreement with the manufacturer’s specification. KOH was used as received.

The reagents were charged into 125-mL stainless steel Teflon-lined autoclaves (Parr Instrument Co., Moline, IL). They occupied about 70% of the volume. The pressure in the vessel was autogenous and can be estimated at 6 atm at 433 K and at 15 atm at 473 K. The experimental setup was designed to avoid temperature gradients within the vessel as described in a previous paper. The vessel was maintained at the experimental temperature (433 or 473 K) for 48–60 h to ensure the complete equilibration. No stirring was employed because it was found to have no influence on the reactions in our system.

Results and Discussion

1. Synthesis in the Region of Thermodynamic Instability of SrZrO$_3$. As expected, the reactions performed in the zero yield area using commercial Sr(OH)$_2$·8H$_2$O in conjunction with HNO$_3$ and CO$_2$-containing hydrous ZrO$_2$ (cf. reaction 1a from Table 3) gave only poorly crystallized ZrO$_2$ (monoclinic, J CPDS No. 37-1484 and tetragonal, J CPDS No. 24-1164), which is due to a transformation of amorphous hydrous ZrO$_2$. Even though both ZrO$_2$ and Sr(OH)$_2$·8H$_2$O contain CO$_2$, SrZrO$_3$ does not precipitate because it is not stable at these low pH values. Reactions performed with Sr(NO$_3$)$_2$ and CO$_2$-containing hydrous ZrO$_2$ also resulted in a mixture of tetragonal and monoclinic ZrO$_2$ (cf. reaction 2a in Table 3). The same reaction was performed with a small amount of KOH (cf. Table 3, reaction 1) in a glovebox and precipitated a mixture of ZrO$_2$ and SrZrO$_3$ (orthorhombic, J CPDS No. 5-418) where the primary source of carbonate was from amorphous ZrO$_2$, indicating that the zirconium precursor can act as a source of contamination of SrZrO$_3$ with carbonates. The above

![Figure 14. Calculated phase stability and yield diagram at 473 K for Sr/Zr = 2.0 using Sr(OH)$_2$ as a source of Sr when the amount of CO$_2$ in the starting materials (i.e., hydrous ZrO$_2$) is equal to 0.036 times the amount of ZrO$_2$. The solid circle denotes experimental conditions for which SrZrO$_3$ contaminated with 2.6 wt % of SrCO$_3$ was obtained.](image)

results are in very good agreement with the predictions of our thermodynamic model which is illustrated in Figure 12 with symbols × and + and in Table 3 (reactions 1a, 2a and 1).

2. Synthesis in the Region of Thermodynamic Stability of SrZrO3 but outside the Complete Yield Region. In the region of incomplete reaction, we have obtained a mixture of SrZrO3 (orthorhombic, JCPDS No. 10-268), SrCO3 and ZrO2 (cf. reactions 2 and 3, Table 3). When Sr(NO3)2 was used in conjunction with a small amount of KOH (cf. reaction 2) or Sr(OH)2·8H2O was used with HNO3 (cf. reaction 3), we obtained SrZrO3 and ZrO2 in varying proportions, depending on the pH, and SrCO3. The detected amounts of SrCO3 agree very well with the amounts predicted by our model assuming that all reagents (i.e., hydrous ZrO2 and KOH or Sr(OH)2·8H2O) contain carbonates. Since all reactions from this region were performed in inert gas atmosphere, it appears that carbonate contamination is mainly due to the CO2 content of starting materials.

3. Synthesis in the Region of Thermodynamic Stability of SrZrO3. As expected, reactions performed in the complete yield region of SrZrO3 gave SrZrO3 and SrCO3 or phase-pure SrZrO3 depending on the purity of precursors. SrZrO3 and SrCO3 were obtained from the reaction 4 (cf. Table 3) which was performed using all CO2-containing reagents. The calculated content of CO2 is 1.9 wt%. TGA analysis shows the decomposition of SrCO3 at approximately 1173–1223 K which is lower than the decomposition of pure SrCO3 (i.e., 1373 K28). This may be caused by the small particle size of hydrothermal SrCO3. The CO2 content calculated from the weight loss and wet chemical analysis is 1.7 and 2.0 wt %, respectively. Similar reactions performed

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a Filtration and washing performed in inert gas.
with lower amounts of KOH and different Sr/Zr ratios also resulted in the formation of SrZrO3 and SrCO3 (cf. Table 3, reactions 5–7). Calculated amounts of CO2 present in SrZrO3 agree very well with those obtained from TGA and wet chemical analysis. It was of interest to repeat the same reactions in air in order to elucidate whether contact with air increases the amount of CO2 in our product. Reactions 3a and 4a are representative for these experiments and can be compared to reactions 5 and 6. As shown in Table 3, no significant influence of air is observed. Reactions performed with CO2-free ZrO2, Sr(NO3)2, and various amounts of commercial KOH gave also SrZrO3 contaminated with SrCO3 (cf. Table 3, reactions 8 and 10). SrCO3 was not detectable by XRD in some cases (e.g., reaction 10) because of its small content in SrZrO3. The calculated amounts of CO2 in SrZrO3 are also in good agreement with those detected by TGA and wet chemical analysis. Products of analogous reactions (cf. reactions 9 and 11) washed and vacuum filtered in inert gas atmosphere show amounts of CO2 that are similar to those in reaction 8 and 10. This confirms our conclusion that carbonate contamination of our product results from the carbonate contamination of precursors. Reactions 12 and 13 were performed using CO2-containing Sr(OH)2·8H2O and ZrO2 without any KOH. According to our calculations, SrZrO3 formed with SrCO3 contamination. Here, the experimental amount of CO2 is somewhat greater than the calculated amount which is probably due to the variation of CO2 content within the large Sr(OH)2·8H2O crystals. Similar reaction (cf. reaction 5a) performed in air did not introduce additional carbonate contamination. Reactions performed with CO2-free Sr(OH)2·8H2O (cf. reactions 6a–9a) resulted in formation of SrZrO3 and SrCO3. In this case, contamination results from carbonate content of hydrous ZrO2, and the agreement between experimental and calculated amounts of CO2 is very good. This may signify that carbonate content of ZrO2 is equally distributed within fine particles of ZrO2 in contrast to the SrCO3 content in Sr(OH)2·8H2O crystals. Finally, reactions performed with CO2-free Sr(OH)2·8H2O and ZrO2 gave phase-pure SrZrO3 as confirmed by TGA and wet chemical analysis (cf. Table 3, reactions 14 and 15). FTIR spectra supported these findings by showing no evidence of carbonates as well. Thus, in this case, we can conclude that we have substantially reduced or eliminated carbonate species, whether they are amorphous or crystalline. The results of our experiments show very good agreement with the predictions of our thermodynamic model. The model is fully validated because it correctly predicts the formation of all phases that are observed in the system and, at the same time, gives their amounts with high accuracy. Selected experimental conditions and produced phases (not necessarily included in Table 3) are also shown in Figures 11–14. The amount of CO2 in Figure 12 corresponds to the average CO2 content in all reactions performed with Sr(NO3)2 at 473 K for Sr/Zr = 1.1. Small variations of carbon dioxide content do not affect the phase boundaries.

4. Physical Characteristics. Characteristic spotted selected area electron diffraction patterns indicated that the particles of SrZrO3 are monocrystalline. The shape of the particles strongly depends on the chemical identity of starting materials. They have diverse shapes with dimensions ranging from 0.2 to 1.5 μm. In particular, cubelike particles are observed when Sr(NO3)2 and KOH are used, rounded shapes are noted if NaOH was used instead of KOH, and clusters of crystallites are obtained from Sr(OH)2·8H2O.

Conclusions

Electrolyte thermodynamics, coupled with a facility for the automatic generation of stability and yield diagrams, provides a powerful tool for predicting the effect of various process conditions on the synthesis of SrZrO3. The model is particularly valuable for analyzing the effects of changing the chemical identity and relative amounts of starting materials as well as for predicting the possibility of contamination with carbonates. The theoretical predictions allow us to formulate synthesis guidelines. These guidelines strongly depend on whether CO2 is present or absent in the starting materials. If the reactants do not contain CO2 and all manipulations are performed in CO2-free atmosphere, it is better to use Sr(OH)2 rather than Sr(NO3)2 with the Sr/Zr ratio varying from 1.2 to 4.4 at T = 433 K and from 1.8 to 2.7 at T = 473 K. The appropriate Sr/Zr ratio ensures that the precipitation of the excess amount of Sr in the form of Sr(OH)2 is avoided. If a certain level of contamination with CO2 cannot be avoided, it is necessary to maintain the Sr/Zr ratio above 1.0. Otherwise, unreacted ZrO2 will remain in the product. It may be then advantageous to use Sr(NO3)2 in conjunction with KOH because Sr(NO3)2 is not likely to contain carbonates. If this is the case, the Sr/Zr ratio between 1.05 and 2.0 is then recommended because it minimizes the necessary amount of KOH. Also, larger amounts of KOH are not advisable because they may cause the precipitation of undesirable Sr(OH)2. Irrespective of whether CO2 is present or not, it is advisable to perform the syntheses at higher temperatures (i.e., 473 as opposed to 433 K) because the 99 mol % yield region field is larger and smaller amounts of KOH are required.

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