Zirconium Titanate from Sol–Gel Synthesis: Thermal Decomposition and Quantitative Phase Analysis

Edgardo L. Sham,* Miguel A. G. Aranda,† E. Mónica Farfan-Torres,* Juan C. Gottifredi,* María Martínez-Lara,† and Sebastián Bruque†.1

*INIQUI, Universidad Nacional de Salta, 177 Buenos Aires, 4400 Salta, Argentina; and †Departamento de Química Inorgánica, Cristalografía y Mineralogía, Universidad de Málaga, 29071 Málaga, Spain

Received December 2, 1997; accepted March 20, 1998

Oxides precursors $\text{Zr}_x\text{Ti}_{1-x}\text{O}_2$ ($x = 0.22, 0.39,$ and $0.60$) were prepared by a hydrolytic sol–gel process. The amorphous mixed oxides are homogeneous as deduced from electron microscopy and XPS studies. The crystallization of these amorphous oxides was studied by TGA–DTA and thermodiffractometry. Quantitative analysis of the crystalline phases, obtained at $1000^\circ \text{C}$, was carried out by the Rietveld method. The samples are mixtures of $\text{TiO}_2$, $\text{Zr}_5\text{Ti}_7\text{O}_{24}$, and $\text{ZrO}_2$ oxides, and the stoichiometry of the oxides precursors $\text{Zr}_x\text{Ti}_{1-x}\text{O}_2$ is formed may be considerably lowered by using a sol–gel process. These initial amorphous oxide precursors $\text{Zr}_x\text{Ti}_{1-x}\text{O}_2$ are prepared by a hydrolytic sol–gel process. These initial solid are characterized by electron microscopy and XPS. The crystallization of these amorphous oxides is studied by TGA–DTA and thermodiffractometric techniques. Quantitative analysis of the high-temperature crystalline phases is carried out by the Rietveld method.

1To whom correspondence should be addressed.
EXPERIMENTAL

Synthesis

To prepare the precursor gels, zirconium n-propoxide (ZNP) (70% in n-propanol) and titanium isopropanoxide (TIP) (97%) were used. Gels with composition Zr\(_x\)Ti\(_{1-x}\)O\(_2\) (\(x = 0.22, 0.39,\) and 0.60) were prepared by mixing 1 M ZNP and TIP n-propanol solutions in the appropriate ratios and stirring for 2 hr at room temperature. Hydrolysis was then carried out by adding water dropwise up to a molar ratio \(\text{H}_2\text{O}/(\text{Zr} + \text{Ti}) = 4\). The obtained gels were refluxed for 24 hr, washed, and dried at 60°C. These samples were ground to white fine powders and are named ZT22, ZT39, and ZT60, respectively (ZTsX). Firing the gels at relatively low temperatures produces the ceramic materials (ZTX). The samples for the Rietveld study were obtained by firing the ZTsX samples at 1000°C.

Characterization

\(\text{TiO}_2\) and \(\text{ZrO}_2\) contents were determined by X-ray fluorescence (XRF) and electron microanalysis (AEM) on samples previously calcined at 1100 and 600°C, respectively. XRF analyses were carried out on a Rigaku Thermoflex 8110 with an electron probe microanalyzer Edax (Si–Li detector). To obtain information on surface chemical composition, the samples calcined at 600°C were also studied by XPS spectrometry. XPS analyses were performed on a Physical Electronics 5700 instrument using a MgK\(\alpha\) X-ray source (1253.6 eV). Accurate (+0.1 eV) binding energies (BE) were determined with respect to the position of the C 1s peak at 284.6 eV.

Thermal analyses (DTA and TGA) of the ZTsX samples were carried out in air on a Rigaku Thermoflex 8110 with a Thermal Station TAS 100 from room temperature to 1100°C at a heating rate of 10 K min\(^{-1}\) with calcined \(\text{Al}_2\text{O}_3\) as standard reference. Powder thermodiffractometric studies of the ZTsX samples were carried out on a Siemens D-5000 diffractometer permanently equipped with an HTK10 heating chamber. The patterns were scanned over the angular range 8–38° (2\(\theta\)), with a step size of 0.04° and counting time of 1 s per step. The appropriate heating and cooling temperatures were selected by using the Diffract AT software. Before any pattern was obtained, a delay time of 10 min was selected to ensure that the transformations took place. Room temperature powder diffraction patterns of the high-temperature calcined phases (ZTX) were collected in a second goniometer of the Siemens D-5000 automated diffractometer using graphite-monochromated CuK\(\alpha\) radiation. To carry out the quantitative phase analysis by the Rietveld method, data were collected between 20° and 70° (2\(\theta\)) with a 0.03° step size and 3-s counting time.

The powder patterns were analyzed by the Rietveld method using the GSAS (21) set of programs. The initial unit cell parameters were as follows: space group \(\text{Pbcn}\), \(a = 4.8\) Å, \(b = 5.5\) Å, and \(c = 5.0\) Å for \(\text{Zr}_{0.4167}\text{Ti}_{0.5833}\text{O}_2\); space group \(\text{P4}_2/mnm\), \(a = 4.611\) Å, and \(c = 2.982\) Å for \(\text{TiO}_2\) (rutile structure); and space group \(\text{P4}_2/\text{nmcm}\), \(a = 3.64\) Å, and \(c = 5.27\) Å for \(\text{ZrO}_2\) (tetragonal structure). These values were optimized in the refinement process. The atomic parameters for each phase are given in Table 1 and they were not refined.

The common overall parameters, histogram scale factor, background coefficients, zero-shift error, and pseudo-Voigt coefficients (\(GW, LY\), and \(LX\)) (22) corrected for asymmetry \((H/L = 0.015, S/L = 0.015)\) (23, 24) were refined first. Then the unit cell parameters were refined. Finally the phase ratio was optimized.

RESULTS

The ZTsX samples are noncrystalline phases and they have different thermal behaviors. The chemical compositions of the samples heated at 600°C were determined by AEM and the results are reported in Table 2. AEM is a statistical

<table>
<thead>
<tr>
<th>Site</th>
<th>symmetry</th>
<th>(x)</th>
<th>(y)</th>
<th>(z)</th>
<th>Fraction</th>
<th>(U_{\text{iso}}(\text{Å}^2))</th>
</tr>
</thead>
<tbody>
<tr>
<td>“Zr(<em>x)Ti(</em>{1-x})O(_2)&quot;</td>
<td>Zr</td>
<td>4c</td>
<td>0.00</td>
<td>0.2030</td>
<td>0.25</td>
<td>0.4167</td>
</tr>
<tr>
<td></td>
<td>Ti</td>
<td>4c</td>
<td>0.00</td>
<td>0.2030</td>
<td>0.25</td>
<td>0.5833</td>
</tr>
<tr>
<td></td>
<td>O</td>
<td>8d</td>
<td>0.2689</td>
<td>0.4024</td>
<td>0.4337</td>
<td>1.00</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Site</th>
<th>Symmetry</th>
<th>(x)</th>
<th>(y)</th>
<th>(z)</th>
<th>Fraction</th>
<th>(U_{\text{iso}}(\text{Å}^2))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zr</td>
<td>4c</td>
<td>0.00</td>
<td>0.2030</td>
<td>0.25</td>
<td>0.4167</td>
<td>0.005</td>
</tr>
<tr>
<td>Ti</td>
<td>4c</td>
<td>0.00</td>
<td>0.2030</td>
<td>0.25</td>
<td>0.5833</td>
<td>0.005</td>
</tr>
<tr>
<td>O</td>
<td>8d</td>
<td>0.2689</td>
<td>0.4024</td>
<td>0.4337</td>
<td>1.00</td>
<td>0.01</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Sample</th>
<th>Ti (metal at.%)</th>
<th>Zr (metal at.%)</th>
<th>(\text{TiO}_2) (metal at.%)</th>
<th>(\text{ZrO}_2) (metal at.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZT22</td>
<td>77.5</td>
<td>22.5</td>
<td>76.6</td>
<td>23.4</td>
</tr>
<tr>
<td>ZT39</td>
<td>58.6</td>
<td>41.4</td>
<td>57.9</td>
<td>42.1</td>
</tr>
<tr>
<td>ZT60</td>
<td>37.8</td>
<td>62.2</td>
<td>39.1</td>
<td>60.9</td>
</tr>
</tbody>
</table>
analysis over individual microparticles. The AEM analyses show that there is no phase segregation in ZTsX solids, the compositions being very homogeneous over all particles. The chemical compositions of the samples heated at 1100°C (determined by XRF) are also presented in Table 2. The results obtained with both techniques are in good agreement, showing that the overall chemical compositions are the same at 600 and 1100°C.

XPS results are listed in Table 3. It can be seen that samples ZT22 and ZT60 present similar Zr 3d, Ti 2p, and O 1s BE. For ZT39, these values are shifted to higher BE. The measured BE are different from those reported in the literature for ZrO₂ (Zr 3d₅/₂ = 182.2 eV, O 1s = 530.2–530.9 eV) and TiO₂ (Ti 2p = 458.7–458.8 eV, O 1s = 529.9 eV), always being shifted to lower values. Moreover, the measured BE do not correspond to those of ZrTiO₄ (Zr 3d₅/₂ = 182.2 eV, Ti 2p = 458.7–459.0 eV, O 1s = 530.2–532.5 eV) (25). The surface chemical compositions found for all samples changes as expected from the initial molar ratios.

The differential thermal analyses in air show the presence of a very strong exothermic peak due to crystallization and/or phase transformation processes. This exotherm takes place without mass changes. The temperatures of this exotherm are 662, 700, and 690°C for ZT22, ZT39, and ZT60, respectively. These are considerably higher than that of pure ZrO₂. It has to be taken into account that these are dynamic values on heating, and therefore the true transformation temperatures have slightly lower values.

The thermodiffractometric studies show that ZT22 crystallizes at approximately 650°C, giving TiO₂ anatase as the main component and Zr₅Ti₇O₂₄ (Fig. 1). The main diffraction peak of anatase is situated at 3.52 Å (25.2° 2θ), PDF no. 21-1272. After this sample was heated at 1000°C, a mixture of TiO₂ (rutile structure), Zr₅Ti₇O₂₄, and ZrO₂ (tetragonal structure) was observed in the XRD profile. These components were identified by their published powder patterns, PDF no. 21-1276, 34-209, and 24-1164, respectively. Due to the strong overlapping of the diffraction peaks, the phase ratio was derived from the Rietveld analysis (see later). ZT39 crystallizes near 700°C, giving mainly Zr₅Ti₇O₂₄ (Fig. 2).
However, a detailed study of the powder pattern of the sample calcined at 1000°C reveals the presence of a tiny amount of rutile. ZT60 crystallization starts at 650°C and it is finished at 700°C (Fig. 3). From the medium-resolution thermomodiffractometric study, only the $\text{Zr}_5\text{Ti}_7\text{O}_{24}$ phase is evident, as $\text{ZrO}_2$ peaks are overlapped down to the $\text{Zr}_5\text{Ti}_7\text{O}_{24}$ major peaks.

The power of the Rietveld method in carrying out a quantitative phase analysis of multiphase samples with strong overlapping is evidenced in this study. The results of the phase analysis are shown in Tables 4 and 5. Table 4 shows the determined weight phase fractions together with the calculated weight fractions derived from the initial composition of the samples (corroborated with the chemical analysis). However, we point out that ZT22 heated at 1000°C is a triphasic sample with $\text{TiO}_2$, $\text{Zr}_5\text{Ti}_7\text{O}_{24}$, and $\text{ZrO}_2$. Thus, it is not possible to calculate the theoretical final composition that will yield $\text{Zr}_{0.22}\text{Ti}_{0.78}\text{O}_2$. To compare the refined values with “some” calculated, we assumed that the final calculated rutile composition was 63.9% and then derived the phase fractions for $\text{Zr}_5\text{Ti}_7\text{O}_{24}$ and $\text{ZrO}_2$. Table 5 shows the refined unit cell and peak shape parameters. The final Rietveld plots are shown in Figs. 4, 5, and 6 for ZT22, ZT39, and ZT60, respectively. $R_{wp}$ ranges between 18 and 22% and $R_p$ ranges between 14 and 16% for the three refined patterns.

**DISCUSSION**

The exothermic peak observed in the DTA can be related to the different phase compositions of the ZTsX samples. For ZT22, the exothermic peak at 662°C is very sharp and strong and is due to the crystallization of the amorphous precursor. It must be mainly related to the formation of $\text{Zr}_5\text{Ti}_7\text{O}_{24}$ because $\text{TiO}_2$ anatase crystallization takes place with minor changes in the DTA. The strong exotherm at 700°C for ZT39 also corresponds to the crystallization of zirconium titanate, in agreement with the DTA results.

**TABLE 4**

Quantitative Crystalline Phase Analysis by the Rietveld Method

<table>
<thead>
<tr>
<th>Sample</th>
<th>Phases</th>
<th>Weight fraction (%)</th>
<th>Determined overall molar ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Zr}<em>{0.22}\text{Ti}</em>{0.78}\text{O}_2$</td>
<td>TiO$_2$</td>
<td>64.3 (fixed)</td>
<td>$\text{Zr}<em>{0.173}\text{Ti}</em>{0.827}\text{O}_2$</td>
</tr>
<tr>
<td>$\text{Zr}_5\text{Ti}<em>7\text{O}</em>{24}$</td>
<td>24.4</td>
<td>23.7</td>
<td></td>
</tr>
<tr>
<td>$\text{ZrO}_2$</td>
<td>11.3</td>
<td>12.0</td>
<td></td>
</tr>
<tr>
<td>$\text{Zr}<em>{0.36}\text{Ti}</em>{0.61}\text{O}_2$</td>
<td>TiO$_2$</td>
<td>5.3</td>
<td>$\text{Zr}<em>{0.402}\text{Ti}</em>{0.598}\text{O}_2$</td>
</tr>
<tr>
<td>$\text{Zr}_5\text{Ti}<em>7\text{O}</em>{24}$</td>
<td>94.7</td>
<td>97.1</td>
<td></td>
</tr>
<tr>
<td>$\text{ZrO}_2$</td>
<td>36.6</td>
<td>38.7</td>
<td></td>
</tr>
<tr>
<td>$\text{Zr}<em>{0.60}\text{Ti}</em>{0.40}\text{O}_2$</td>
<td>$\text{Zr}_5\text{Ti}<em>7\text{O}</em>{24}$</td>
<td>63.4</td>
<td>$\text{Zr}<em>{0.612}\text{Ti}</em>{0.388}\text{O}_2$</td>
</tr>
<tr>
<td></td>
<td>ZrO$_2$</td>
<td>36.6</td>
<td></td>
</tr>
</tbody>
</table>
reported for gels prepared by hydrolysis of metal alkoxides (26). For ZT60, the exothermic change takes place at 690°C.

The thermodiffractometric study indicates that the samples calcined at 600°C are amorphous, and the AEM and XPS studies confirm that they are mixed oxides. The samples cannot also be a mixture of amorphous oxides or ZrTiO₄ because the Ti 2p and Zr 3d measured BE do not correspond to those of either the isolated oxides or ZrTiO₄. Upon crystallization, phase segregation takes place as shown by thermodiffractometry.

The refined phase ratios (Table 4) are in good agreement with those expected from the initial compositions. Average errors of the order of 2% have been found in this study, which are low taking into account the large overlapping between diffraction peaks worsened by the broad peaks shown by some phases. We emphasize that the stoichiometry found for the zirconium titanate phase is invariably Zr₅Ti₇O₂₄. If the Rietveld refinements are carried out with the stoichiometry ZrTiO₄, for zirconium titanate, R_w only worsens (increases) by 0.5% but the determined phase ratios make no sense.

Quantitative phase analysis by the Rietveld method requires stoichiometric phases for the simulation of the theoretical profiles. As shown by the unit cell values of TiO₂ (Table 5), this phase is very crystalline (sharp peaks), with the refined unit cell parameters very close to those reported

\[
\begin{align*}
\text{TABLE 5} & \quad \text{Refined Unit Cell and Peak Shape Parameters for the Final Rietveld Refinements} \\
\hline
\text{Sample} & \text{Phases} & a (\text{Å}) & b (\text{Å}) & c (\text{Å}) & V (\text{Å}^3) & L_Y (\text{deg}) \\
\hline
Zr₀.₃₂Ti₀.₇₈O₂ & TiO₂ & 4.6118(3) & 4.6118 & 2.9817(2) & 63.42(1) & 0.058(16) \\
Zr₀.₃₂Ti₀.₇₈O₂ & Zr₂O₃ & 4.800(4) & 5.457(4) & 5.027(4) & 131.7(1) & 1.48(7) \\
Zr₀.₃₂Ti₀.₇₈O₂ & Zr₂O₃ & 3.57(1) & 3.57(1) & 5.22(2) & 66.60(3) & 0.88(4) \\
Zr₀.₃₂Ti₀.₇₈O₂ & TiO₂ & 4.6114 & 4.6114 & 2.9817 & 63.41 & 0.53(1) \\
Zr₀.₃₂Ti₀.₇₈O₂ & Zr₂O₃ & 4.765(1) & 5.473(1) & 5.018(1) & 130.85(7) & 1.02(1) \\
Zr₀.₃₂Ti₀.₇₈O₂ & Zr₂O₃ & 4.862(3) & 5.403(3) & 5.033(3) & 132.2(1) & 1.59(5) \\
Zr₀.₃₂Ti₀.₇₈O₂ & TiO₂ & 3.558(2) & 3.558 & 5.262(3) & 66.62(7) & 1.76(5) \\
\end{align*}
\]

*LX was also refined: 0.071(5)*.
FIG. 4. Observed, calculated, and difference X-ray diffraction plots for Zr$_{0.22}$Ti$_{0.78}$O$_2$ (ZT22) calcined at 1000°C. Reflection positions for Zr$_5$Ti$_7$O$_{24}$ (bottom), TiO$_2$ (center), and ZrO$_2$ (top) are marked.

FIG. 5. Observed, calculated, and difference X-ray diffraction plots for Zr$_{0.39}$Ti$_{0.61}$O$_2$ (ZT39) calcined at 1000°C. Reflection positions for Zr$_5$Ti$_7$O$_{24}$ (bottom) and TiO$_2$ (top) are marked.
in the literature. However, some slight deviations from stoichiometry may occur for Zr$_{5}$Ti$_{7}$O$_{24}$ and ZrO$_{4}$ (tetragonal). As shown in Table 5, the refined volumes of these phases show some small variations. This implies some errors in the refined compositions that would explain the slight disagreement between starting and refined compositions. Furthermore, the presence of amorphous oxides is not taken into account by this type of Rietveld analysis. However, the close relationship between the overall starting compositions and the overall refined metal ratios suggests that amorphous phases are negligible in these systems.

Finally, we emphasize that the peak shapes vary considerably for different phases and samples. For a given firing temperature, zirconium-rich phases show broader peaks. ZT60 heated at 1000°C presents very broad peaks (Fig. 6, Table 5) due to lattice microstrain rather than microparticle-related broadening. This is due to some local deviation from ideal stoichiometry in the microcrystallites.

ACKNOWLEDGMENTS

The cooperation between Málaga and Salta has been financed by AECI through the “Programa de Cooperación con Iberoamérica (Ministerio de Asuntos Exteriores, España).” This work was also supported by research grant FQM-113 from the Junta de Andalucía (Málaga) and the PID-BID CONICET IO-305 Project (Salta).

REFERENCES