Atomic-Scale Structure of Al$_2$O$_3$-ZrO$_2$ Mixed Oxides Prepared by Laser Ablation

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Abstract. By means of x-ray diffractometry (XRD) and X-ray absorption fine structure spectroscopy, the phase composition and atomic structure of laser evaporated ZrO$_2$ and ZrO$_2$-Al$_2$O$_3$ nanopowders have been studied. The results indicate that pure ZrO$_2$ exists in the form of tetragonal structure, Al$_2$O$_3$ doped ZrO$_2$ nanoparticles, however, have cubic structure. Compared to bulk tetragonal ZrO$_2$, pure tetragonal ZrO$_2$ nanoparticles have a shorter Zr-O- and Zr-Zr shell, indicating that the lattice contracts with decreasing particle size. For Al$_2$O$_3$ doped ZrO$_2$ solid solution, the distances of first Zr-O and Zr-Zr (Al) coordination decrease with increasing solid solubility. The disorder degree of the ZrO$_2$ lattice increases with increasing solid solubility. The coevaporated ZrO$_2$-Al$_2$O$_3$ is quickly solidified into amorphous phase when it is ablated in a higher pressure. The amorphous phase contains Zr-O-Zr (Al) clusters and has shorter Zr-O distance and lower Zr-O coordination number.

Keywords: laser evaporation, nanoscale particles, ZrO$_2$-Al$_2$O$_3$ solid solution, XAFS, XRD.

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ZrO$_2$ based ceramics has been widely used for oxygen sensors, high-temperature fuel cells, thermal barrier coatings, catalyst supports and toughened ceramics. A special interest is being given to ZrO$_2$–Al$_2$O$_3$ system because of its importance [1]. The phase diagrams [2] of ZrO$_2$-Al$_2$O$_3$ system show that the largest solid solubility of Al$_2$O$_3$ in ZrO$_2$ is about 7 mol % even if it is annealed at 2183K because Al$^{3+}$ is apparently too small to substitute extensively for Zr$^{4+}$. However, Balmer et al. [3] synthesized ZrO$_2$-Al$_2$O$_3$ solid solutions with up to 40 mol % Al$_2$O$_3$ by the simultaneous hydrolysis of zirconium and aluminum alkoxides; Yamaguchi et al. [4] reported that single-phase c-ZrO$_2$ solid solutions containing up to 45 mol% Al$_2$O$_3$ could be synthesized by spray pyrolysis. We also synthesized ZrO$_2$-Al$_2$O$_3$ solid solution with up to 33 mol % Al$_2$O$_3$ by laser ablation [5]. Though the Al$_2$O$_3$ solubility depends on the synthesis method and condition, the structural organization of these metastable phases remains poorly understood. In the present work, the phase composition and atomic structure of nanometer ZrO$_2$ and ZrO$_2$-Al$_2$O$_3$ mixtures have been investigated by means of XRD and XAFS spectroscopy in order to further understand the structural organization of these metastable phases.

ZrO$_2$ and ZrO$_2$-Al$_2$O$_3$ nanopowders were prepared by laser evaporation of compressed micrometer powders using a 400 W Nd:YAG laser (wavelength=1.06 μm) and subsequent recondensation of the laser-induced vapor in air or argon atmospheres at different pressures by changing the flow rate of the introduced gas. Nanoparticles generated by gas-phase condensation were collected on a glass fiber filter with an average pore size of several micrometers at room temperature when the aerosol was pumped out of the evaporation chamber. The setup diagram can be found in a previous article [5].

XRD patterns of the collected nanopowders were recorded using a Siemens x-ray diffractometer with CuKα radiation produced with 40 KV and 30 mA. Local structure of the nanoparticles was investigated by a room temperature EXAFS technique. Zr K-edge (17998 eV) XAFS spectra were measured at beamline X1 in transmission mode at HASYLAB in Hamburg, Germany, utilizing a Si (311) double-crystal monochromator. Harmonic rejection was achieved by detuning the monochromator crystals between 40% and 50%. The energy calibration of the monochromator was checked using a Zr metal foil at the K-edge energy of 17998 eV for each experimental measurement. The software package UWXAFS 3.0 [6]
was used to extract the EXAFS oscillation, χ(k), from the raw Zr K-edge x-ray absorption data. The χ(k) was weighted by k² and Fourier transformed using a Hanning window function. For pure t-ZrO₂, the fitted k and R ranges are 3-16 Å⁻¹ and 1.0-4.0 Å, respectively. For the ZrO₂-Al₂O₃ system, the fitted k and R ranges are 3-13 Å⁻¹ and 1.0-4.0 Å, respectively. The uncertainty of interatomic distance is ±0.006 Å.

Fig. 1 gives the XRD pattern of pure t-ZrO₂ nanopowder. The nanopowder was obtained by laser ablating m-ZrO₂ micropowder in air of 9×10⁻⁴ Pa. According to Scherrer formula, the mean crystalline diameter is about 9.1 nm.

Fig. 2 gives the Fourier transform of the Zr K-edge EXAFS spectrum of pure ZrO₂ nanopowder. The first peak in Fig. 2 corresponds to the nearest neighbor Zr-O shell. The second peak corresponds to the next-near neighbor Zr-Zr shell. Others probably correspond to the outer Zr-Zr shells since the outer Zr-O shells are not expected due to the weak scattering function of oxygen.

Fig. 3 gives the Fourier transforms of Zr K-edge EXAFS spectra of the samples NS1, NS2 and NS3. The samples NS1 and NS2 were prepared from mixtures of 28.5 mol% α-Al₂O₃–71.5 mol% m-ZrO₂ and 31.0 mol% α-Al₂O₃–69 mol% m-ZrO₂ by laser ablation in air atmosphere (9×10⁻⁴ Pa), respectively. The sample NS3 was prepared from mixture of 33.0 mol% α-Al₂O₃–67 mol% m-ZrO₂ by laser ablation in argon atmosphere (9×10⁻⁴ Pa). Our previous research [5] shows that the solubility limit of Al₂O₃ in ZrO₂ is about 28 mol% in air atmosphere of 9×10⁻⁴ Pa. However, the solid solubility limit of Al₂O₃ in ZrO₂ is about 33 mol% if the nanopowder is prepared in argon atmosphere of 9×10⁻⁴ Pa.

Fig. 4 gives XRD patterns of the samples NSA, NSB, NSC and NSD, which were prepared from mixture of 50 mol% α-Al₂O₃–50 mol% m-ZrO₂ by laser ablation at different air pressures (p).

The first peak in Fig. 2 corresponds to the nearest neighbor Zr-O shell. The second peak corresponds to the next-near neighbor Zr-Zr shell. Others probably correspond to the outer Zr-Zr shells since the outer Zr-O shells are not expected due to the weak scattering function of oxygen.

Fig. 3 shows that the magnitude of the Zr–Zr (Al) shell decreases dramatically compared to that of pure nanometer t-ZrO₂ in Fig. 2. The reasons are: (a) Al atoms dissolved into ZrO₂ crystalline lattices have a much lower backscattering factor compared to Zr atoms; (b) The disorder degree increases with the solid solution concentration of Al₂O₃ in ZrO₂.

Fig. 4 shows that NSA and NSB mainly consist of c-ZrO₂ and γ-Al₂O₃. In NSC and NSD the diffraction
peaks of ZrO$_2$ disappear nearly and the intensity of Al$_2$O$_3$ diffraction peaks drastically decreases, indicating that NSC and NSD both mainly consist of amorphous phases. This can be attributed to the higher air pressure in the chamber during preparation of NSC and NSD because the laser-induced vapor is quickly condensed into amorphous phases at a higher air pressure.

Fig. 5 gives the Fourier transforms of Zr-K-edge EXAFS spectra of samples NSA, NSB, NSC and NSD. Table 1 lists EXAFS analysis results of the measured samples.

### FIGURE 5.
Fourier transforms of Zr K-edge EXAFS spectra of the ZrO$_2$-Al$_2$O$_3$ nanocomposite powders. Dot curve is fit calculated by UXAFS 3.0.

#### TABLE 1. EXAFS results of nano-ZrO$_2$ and ZrO$_2$-Al$_2$O$_3$ composite powders

<table>
<thead>
<tr>
<th>Sample</th>
<th>R/Å</th>
<th>CN</th>
<th>$\sigma^2$/Å$^2$</th>
<th>R/Å</th>
<th>CN</th>
<th>$\sigma^2$/Å$^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nano-ZrO$_2$</td>
<td>2.242</td>
<td>4.5±1.3</td>
<td>0.0079</td>
<td>3.662</td>
<td>10.4±2.1</td>
<td>0.0069</td>
</tr>
<tr>
<td>NSA</td>
<td>2.174</td>
<td>5.9±0.7</td>
<td>0.010</td>
<td>3.550</td>
<td>9.6±5.5</td>
<td>0.0260</td>
</tr>
<tr>
<td>NSB</td>
<td>2.173</td>
<td>5.9±0.7</td>
<td>0.010</td>
<td>3.548</td>
<td>9.0±5.3</td>
<td>0.0262</td>
</tr>
<tr>
<td>NSC</td>
<td>2.168</td>
<td>6.3±0.7</td>
<td>0.0106</td>
<td>3.530</td>
<td>9.3±5.9</td>
<td>0.0276</td>
</tr>
<tr>
<td>NSD</td>
<td>2.156</td>
<td>6.4±0.7</td>
<td>0.0109</td>
<td>3.521</td>
<td>9.2±5.3</td>
<td>0.0286</td>
</tr>
<tr>
<td>NS1</td>
<td>2.198</td>
<td>7.2±0.8</td>
<td>0.0115</td>
<td>3.589</td>
<td>7.2±1.8</td>
<td>0.0095</td>
</tr>
<tr>
<td>NS2</td>
<td>2.198</td>
<td>7.0±0.7</td>
<td>0.0108</td>
<td>3.589</td>
<td>6.8±1.8</td>
<td>0.0113</td>
</tr>
<tr>
<td>NS3</td>
<td>2.203</td>
<td>6.8±0.6</td>
<td>0.0110</td>
<td>3.597</td>
<td>7.0±1.8</td>
<td>0.0125</td>
</tr>
</tbody>
</table>

The Zr-O coordination numbers are all around 7 in samples NS1, NS2 and NS3, indicating the existence of oxygen vacancy. NS3 has a higher solid solubility of Al$_2$O$_3$ in ZrO$_2$ than NS1 and NS2, thus its Zr–Zr (Al) peak should be lower than that of NS1 and NS2, and its disorder degree of Zr–Zr (Al) coordination should be larger than that of NS1 and NS2. This has been demonstrated by the Debye-Waller factors of Zr–Zr (Al) coordination, 0.0095 Å$^2$ for NS1, 0.0113 Å$^2$ for NS2 and 0.0125 Å$^2$ for NS3. However, increasing the solid solution amount does not affect the magnitude of the Zr-O shell noticeably. For example, the Debye-Waller factors of Zr-O shells are 0.0108 Å$^2$ for NS1, 0.0115 Å$^2$ for NS2 and 0.0110 Å$^2$ for NS3. The Zr-O distances in NSA, NSB, NSC and NSD are 2.174 Å, 2.173 Å, 2.162 Å and 2.156 Å, respectively. Their Zr-O coordination numbers are around 6. NSA and NSB have nearly the same Zr-O distance, and smaller than that of NS1, NS2 and NS3. The Zr-O distance decreases with increasing the content of amorphous phase. In NSD, the crystalline ZrO$_2$ is not detectable, but the corresponding Zr-Zr (Al) peak indicates the existence of Zr-O-Zr (Al) clusters in NSD.

In summary, pure nanometer ZrO$_2$ with mean size of 9.1 nm exists in the form of tetragonal structure. However, Al$_2$O$_3$ doped ZrO$_2$ nanometer crystals have cubic structure. For Al$_2$O$_3$ doped ZrO$_2$ solid solution, the distances of first Zr-O- and Zr-Zr (Al) shells decrease with increasing the solid solution content, and the disorder degree of ZrO$_2$ lattice increase with increasing solid solubility. Binary compound of ZrO$_2$-Al$_2$O$_3$ forms amorphous phase when it is ablated in a higher pressure. The amorphous phase contains Zr-O-Zr clusters and has shorter Zr-O distance and lower Zr-O coordination number.

### ACKNOWLEDGEMENTS
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### REFERENCES

2. Phase Diagrams for Ceramics, National Institute of Standards and Technology, The American Ceramic Society, Inc., Al$_2$O$_3$-ZrO$_2$ Fig. 4377, 4378, 6452.