

Zirconium Oxide: Rietveld and Reverse Monte Carlo Analyses

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The amorphous-to-cubic (a-c) crystallization of nanoZrO₂ in a reducing environment was studied by synchrotron X-ray diffraction. Rietveld analysis was performed to study the changes in crystallite size and lattice parameter as the cubic phase emerged. The pair distribution function (PDF) was obtained from the Fourier transformation of the normalized XRD patterns. A reverse Monte Carlo (RMC) simulation was applied to provide details of the local structure during the crystallization process as well as to calculate partial PDFs of Zr-Zr and Zr-O during the crystallization. The number of Zr's next-nearest neighbors of Zr remains 12, whereas the number of O's as nearest neighbors of Zr increases from 6.7 to 7.3 as the material evolves from an amorphous into a cubic structure, suggesting the persistence of a high concentration of oxygen vacancies. These simulated atomic structures show that the local structure of the amorphous phase bears resemblance to the short-range arrangement of cubic ZrO₂, consistent with the results of X-ray absorption near edge spectroscopy (XANES) at Zr L_{II} and L_{III}. The amorphous-to-crystalline phase transformation is affected by the environment. Under an oxidizing condition, the amorphous phase crystallizes directly to tetragonal and subsequently to monoclinic zirconia.