

Zirconia and titania nanoparticles studied by electric hyperfine interactions, XRD and TEM

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Available online 29 September 2006

Abstract

Nanocrystalline ZrO₂ and TiO₂ (n-ZrO₂, n-TiO₂), synthesized in a microwave plasma, have been investigated by X-ray and electron diffraction and by perturbed angular correlation (PAC) measurements of the nuclear electric quadrupole interaction (QI) of the probe nucleus ¹⁸¹Ta residing on the cation site. The microwave synthesis produces zirconia in the cubic/tetragonal phase, titania in the anatase structure. Grain growth and phase transformations have been studied in bare and Al₂O₃-coated zirconia particles. Coating the nanoparticles with an *amorphous* Al₂O₃ layer obstructs grain growth and may suppress the monoclinic phase.

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Keywords: Nanostructures; Crystal structure and symmetry; Scanning and transmission microscopy

1. Introduction

The interaction between a nuclear electric quadrupole moment Q and the tensor of the electric-field gradient (EFG) at the nuclear site is determined by the charge distribution surrounding the probe nucleus. Because of the r^{-3} -dependence of the EFG the main contributions come from the nearest neighbor charges. Strength and symmetry of the nuclear electric quadrupole interaction (QI) therefore provides information on the structure of the solid on a nanometer scale and complements the structural information on nanoscaled solids obtained from X-ray and electron diffraction. We are presently engaged in a program in which structure, grain growth and phase transformations of nanocrystalline (n) ceramics are investigated by perturbed angular correlation (PAC) measurements [1] of electric quadrupole interactions, X-ray diffraction and transmission electron microscopy. In this contribution, we present some results for n-ZrO₂ and n-TiO₂.

2. Experimental

Nanosized samples of bare ZrO₂ and TiO₂ (n-ZrO₂, n-TiO₂) as well as Al₂O₃-coated n-ZrO₂ and n-TiO₂ with sizes typically <5 nm were synthesized

using the Karlsruhe microwave plasma process (KMPP). This process is a gas phase process capable of producing bare and coated particles [2,3] with a narrow particle size distribution [4]. Using a microwave plasma discharge and an Ar/20 vol.%O₂ gas mixture as reaction gas, evaporated water free precursors (Ti(OC₄H₉)₄, Zr(OC₄H₉)₄, AlCl₃) react to nanosized oxides at $T \leq 900$ K. The relatively low temperatures avoid sintering of the particles and the evolution of hard agglomerates. The coating of single particles is realized by using two plasma stages consecutively in a closed system. The synthesized powders are collected by thermophoresis.

The particles were characterized in the as-synthesized state by X-ray diffraction (XRD) and transmission electron microscopy (TEM) (Figs. 1 and 2). XRD was carried out with a Philips (X'Pert) diffractometer using Cu K α radiation at 50 kV and 40 mA on non-compacted powder samples. Grain growth and phase evolution were studied by room temperature XRD measurements of powders annealed in air for 6 h at different temperatures (Fig. 3).

Electron microscope and electron diffraction patterns of powder samples on holey carbon copper grids were recorded with a Philips (CM-30 ST or Tecnai F20 ST) transmission electron microscope.

The PAC measurements were carried out with the 133–482 keV cascade of ¹⁸¹Ta which is populated in the β^- decay of the 45d isotope ¹⁸¹Hf. In the synthesis the nanoparticles were doped with the stable isotope ¹⁸⁰Hf by adding about 4 at.% of the corresponding Hf precursor. For the generation of the ¹⁸¹Hf/¹⁸¹Ta probe nuclei, non-compacted powder was enclosed under vacuum into quartz tubes and irradiated in a flux of thermal neutrons of 5×10^{13} n/(s cm²) for times of the order of 24 h. The PAC spectra were taken with a standard four-detector setup equipped with fast BaF₂ scintillators as a function of temperature in the range $290 \text{ K} \leq T_M \leq 1500 \text{ K}$. In the study reported here, the samples were cycled between room-temperature and increasing values of T_M . In Fig. 4, the room temperature PAC spectra of ¹⁸¹Ta in coarse grained ZrO₂ and TiO₂ are compared to those of bare and coated nano-oxides. Fig. 5 illustrates the thermal evolution of the PAC spectra, using n-ZrO₂ and n-ZrO₂/Al₂O₃ as examples.

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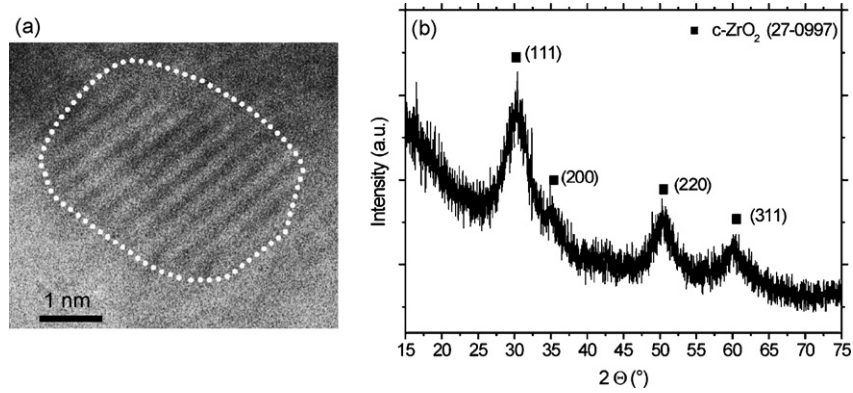


Fig. 1. Electron micrograph (a) and X-ray diffraction (b) of bare n-ZrO₂. For comparison *hkl*-values of c-ZrO₂ (JCPDS card no. 27-0997) are given in (b).

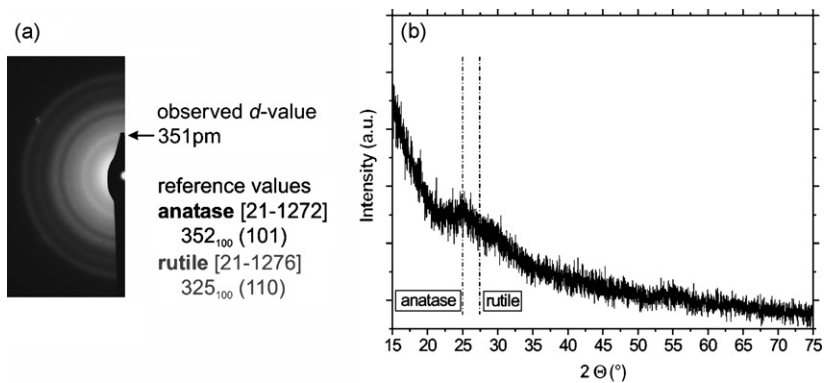


Fig. 2. Electron diffraction (a) and X-ray diffraction (b) of bare n-TiO₂. For comparison *d*-values of reference anatase (JCPDS card no. 21-1272) and rutile (JCPDS card no. 21-1276) structure are given.

3. Results and discussion

The electron and X-ray diffraction data (Figs. 1 and 2) clearly show that the structure of the as-synthesized powders differs from that usually observed in the bulk material at room temperature: n-ZrO₂ is in the cubic or tetragonal rather than the monoclinic phase, n-TiO₂ has the anatase rather than the rutile

structure. This reverse phase stability at very small particle sizes is described by several authors [for TiO₂ see e.g. 5–7]. It can be attributed to the fact that the possible phases differ in the surface contribution to the free energy. As the relative surface

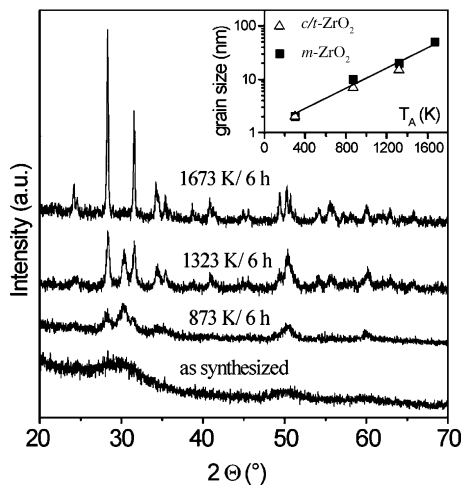


Fig. 3. Room temperature X-ray diffraction pattern of n-ZrO₂ as synthesized and after annealing for 6 h at the temperatures given. The insert shows the grain size as a function of the annealing temperature.

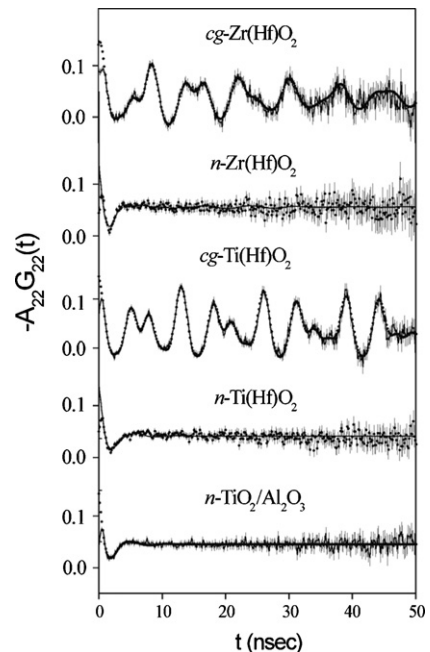


Fig. 4. ¹⁸¹Ta PAC spectra in coarse-grained (cg-) and nanocrystalline n-ZrO₂ and n-TiO₂ at 300 K.

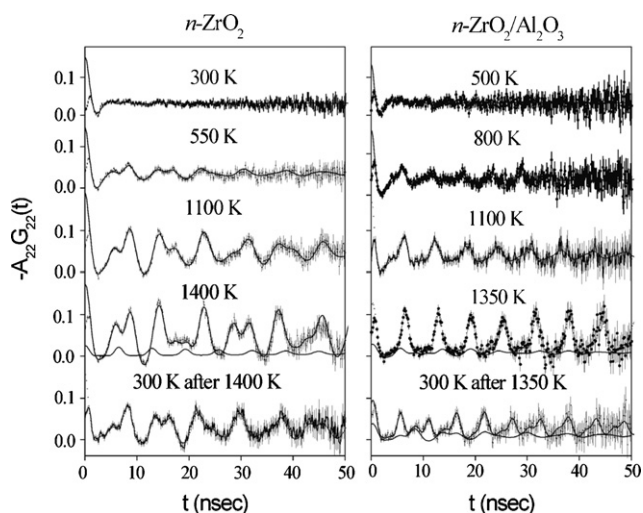


Fig. 5. PAC spectra of ^{181}Ta in bare and Al_2O_3 -coated ZrO_2 nanoparticles at different temperatures.

part increases with decreasing particle size, the phase stability in the nm-range may differ from that of the coarse grained (cg-) material [see e.g. 8,9]. In the TEM micrographs which basically reflect the cation sub-lattice, one recognizes a fairly well established long range order. Fig. 3 illustrates the changes of the XRD spectra of $n\text{-ZrO}_2$ upon annealing. The annealing process leads to (i) the transformation of the initially c/t -phase to monoclinic ZrO_2 and (ii) to grain growth, shown by the decrease of the line width of the X-ray peaks with increasing annealing temperature T_A . The insert shows the grain size determined from the line width using the Scherrer-formula [10]. The exponential increase of the grain size with increasing T_A corresponds to a grain growth activation enthalpy of $Q_A \sim 30$ kJ/mol, in fair agreement with the result of Siu et al. [11] for $n\text{-ZrO}_2$ prepared by the hydrothermal method. Similar annealing experiments for Al_2O_3 -coated ZrO_2 and $n\text{-TiO}_2$ are under way.

In Fig. 4 we compare the ^{181}Ta PAC spectra of $n\text{-ZrO}_2$, bare and Al_2O_3 -coated $n\text{-TiO}_2$ to those of the corresponding coarse-grained material. In the case of cg- ZrO_2 and cg- TiO_2 the time spectrum of the anisotropy shows the well-known non-periodic oscillatory structure typical for the axially asymmetric QI of $m\text{-ZrO}_2$ [12] and rutile TiO_2 [13], respectively. In the nanocrystalline powders, however, the oscillations of the anisotropy are completely wiped out. This is a clear indication that the probe nuclei no longer experience a single well-defined electric field gradient (EFG), but are subject to a broad distribution of different QI's. Because of the r^{-3} dependence of the EFG, the measurements of the QI mainly sample the charge distribution of the nearest-neighbor environment of the probe nucleus. In ZrO_2 and TiO_2 , oxygen ions are the nearest neighbors of the metal sites. The broad QI distribution seen by ^{181}Ta on the Zr- or Ti-site therefore implies a high degree of disorder of the oxygen sublattice which contrasts with the long-range order of the cation sublattice seen in TEM micrographs.

Upon annealing, the broad QI distribution characteristic for the nanoparticles in the as-synthesized state evolves towards a well defined QI. This gradual transition is illustrated in Fig. 5 for $n\text{-ZrO}_2$ and $n\text{-ZrO}_2/\text{Al}_2\text{O}_3$. In bare $n\text{-ZrO}_2$, one first finds the

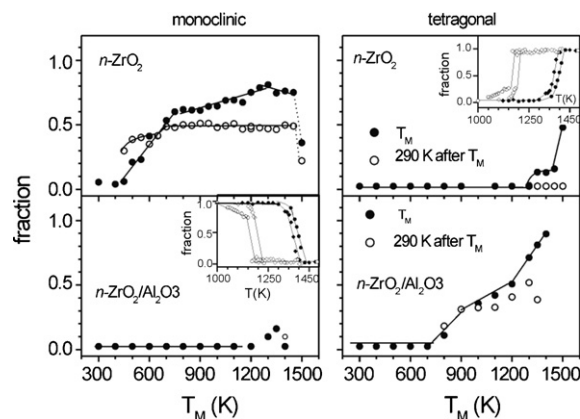


Fig. 6. The thermal evolution of the monoclinic and the tetragonal phase in bare and Al_2O_3 -coated ZrO_2 nanoparticles, observed by ^{181}Ta PAC spectroscopy. The inserts show the $m \leftrightarrow t$ transitions of bulk ZrO_2 .

non-periodic oscillation of monoclinic ZrO_2 and an admixture of the periodic pattern of tetragonal ZrO_2 is observed only at $T \geq 1400$ K. In coated $n\text{-ZrO}_2/\text{Al}_2\text{O}_3$, it is the tetragonal phase which first appears upon heating, the monoclinic phase is suppressed practically up to $T \sim 1350$ K. The relative intensities of the monoclinic and the tetragonal phase in the spectra of Fig. 5 have been extracted using standard PAC analysis. The results are collected in Fig. 6 and compared (see inserts) to the phase transformations in the bulk material. In non-coated $n\text{-ZrO}_2$ the monoclinic phase develops gradually. The transformation to the tetragonal phase occurs at about the same temperature and is as sharp as in cg- ZrO_2 . An interesting result which asks for further investigation is the observation that upon cooling to 300 K the relative intensity of the monoclinic phase is significantly reduced. This reduction implies that at 300 K a part of the probe nuclei is subject to another unresolved high frequency QI. The fact that this reduction does not occur in the bulk material suggests a relation of this phenomenon to the interfacial region of the nanoparticles.

A comparison between the PAC spectra of ^{181}Ta in $n\text{-ZrO}_2$ and $n\text{-ZrO}_2/\text{Al}_2\text{O}_3$ (Fig. 5) and the corresponding relative phase intensities (Fig. 6) clearly shows that a coating of the particles with amorphous Al_2O_3 strongly affects the phase transformations in nanocrystalline zirconia. In contrast to non-coated zirconia, at $T > 700$ K the content of tetragonal ZrO_2 increases continuously, while the monoclinic phase is almost entirely suppressed. The difference can be attributed to the volume expansion of $\sim 4.5\%$, which accompanies the tetragonal-monoclinic transformation in zirconia. In particles mechanically confined by an Al_2O_3 coating, this expansion leads to compressive stresses which stabilize the tetragonal phase. Akin to the obstructed phase transformations, the grain growth of the coated particles is hindered, too. The coated material exhibits $\sim 40\%$ of the particle size of their uncoated counterparts after annealing under similar conditions.

4. Conclusion

The combination of electron and X-ray diffraction with measurements of electric quadrupole interactions allows comple-

mentary insights into structure, phase transition and grain growth of ceramic nanoparticles as zirconia, titania and others. The diffraction methods reflect the degree of long-range order of the cation sublattice, the electric quadrupole interaction samples the charge distribution surrounding the metal sites and therefore provides information on the order of the oxygen sublattice.

The microwave plasma synthesis of ZrO_2 and TiO_2 leads to the cubic/tetragonal and the anatase rather the monoclinic and rutile structure, respectively, usually found in the coarse-grained oxides. With increasing temperature, grain growth and phase transformations have been observed. For n- ZrO_2 the grain growth activation enthalpy has been determined. Coating the particles with amorphous Al_2O_3 , suppresses the monoclinic phase in zirconia and also obstructs grain growth.

Acknowledgements

The authors gratefully acknowledge the financial support by Deutsche Forschungsgemeinschaft (grant numbers VO861/1-1,2 and FO148/3-1,2).

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