

Inhomogeneous depletion of oxygen ions in metal oxide nanoparticles



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ABSTRACT

Zirconia and yttria stabilized zirconia (YSZ) have multiple uses, including catalysis, fuel cells, dental applications, and thermal coatings. We employ nuclear reaction analysis to determine elemental composition of YSZ nanoparticles synthesized by laser evaporation including ¹⁸O studies to distinguish between oxide and adsorbed oxygen content as a function of surface area. We see dramatic deviation from stoichiometry that can be traced to loss of oxygen from the oxide near the surface of these nanopowders. Density functional calculations are coupled with these experimental studies to explore the electronic structure of nonstoichiometric surfaces achieved through depletion of oxygen. Our results show oxygen-depleted surfaces present under oxygen potentials where stoichiometric, oxygen-terminated surfaces would be favored thermodynamically for crystalline systems. Oxygen depletion at nanopowder surfaces can create effective two-dimensional surface metallic states while maintaining stoichiometry in the underlying nanoparticle core. This insight into nanopowder surfaces applies to dissimilar oxides of aluminum and zirconium indicating synthesis conditions may be more influential than the inherent oxide properties and displaying need for distinct models for nanopowders of these important engineering materials where surface chemistry dominates performance.

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1. Introduction

Physical and chemical properties of oxide nanopowders and methods for their synthesis have been the subject of numerous studies. These appear in diverse fields, including catalysis, medicine, and electrochemical devices. In addition to practical applications, such studies hold fundamental implications for understanding the surface physics and chemistry of oxide materials as well as the nature of their magnetic and electronic properties. An important characteristic of oxide nanopowders is their chemical composition. Of particular interest is deviation from stoichiometry and the extent and location of oxygen vacancies in nanoparticles since this presents dramatic consequences for the resulting electronic structure.

There is evidence of deviation from stoichiometry in nanoscale oxide semiconductors and dielectrics even though these exhibit stoichiometric composition in larger scale grains and crystalline solids. Generally, stoichiometric deviation is determined indirectly by characterizing ferromagnetic states in nanopowders or thin films of oxides containing no magnetic dopants. This effect has been observed in a variety of metal oxides, including TiO₂, Al₂O₃, CeO₂, ZnO, In₂O₃, HfO₂, CuO, and Cu₂O [1–10]. The authors of these studies speculate that ferromagnetism of nanoscale oxides is due to oxygen deficiency. The prevailing interpretation is that vacancies are formed in the oxygen sublattice of oxides located in the outer surface layer of nanoparticles or films, i.e., these

results indirectly point to inhomogeneous distribution of oxygen ions in oxide nanoparticles.

In theory as well as practical application, direct measurements of oxygen content in nanopowders provides essential complement to the indirect evidence of oxygen-depleted surfaces. We used nuclear reaction analysis (NRA) to quantify elemental composition of aluminum oxide nanoparticles whose oxygen sublattice is enriched with ¹⁸O isotope [11]. NRA is employed as an alternative to electron spectroscopy methods [12–15] which may require preparation of a clean and homogeneous surface with certified structure. Such ideal surfaces generally cannot be ensured in the examination of nanoparticles; they are difficult to prepare even for monocrystals. The indirect signatures suggesting oxygen deficiency localized to the outer atomic layers in Al₂O₃ nanoparticles comprised of γ , δ , and amorphous phase were confirmed directly in our previous work [11]. Earlier characterization of higher symmetry α -Al₂O₃ crystals, including low-energy electron diffraction [16], grazing incidence x-ray diffraction [17], dynamic scanning force microscopy [18], non-contact atomic force microscopy, and density functional theory (DFT) calculations [19–21], shows that an oxygen-deficient surface reconstruction can be achieved under appropriate pressure and temperature conditions and then persist at ambient conditions where that surface is not thermodynamically favored. This $\sqrt{31} \times \sqrt{31} R^{\circ}$ reconstruction is achieved through loss of two oxygen layers from the stoichiometric surface, i.e., two O₃ units from the “Al–O₃–Al–Al–O₃–Al...” surface.

Relaxation of the remaining surface aluminum results in a thin layer of effectively Al(111) over a stoichiometric Al_2O_3 substrate.

At present, there is considerable indirect evidence of stoichiometric deviation in oxide nanopowders but only in our previous alumina study was this quantified directly, including oxygen isotope concentrations. A fundamental understanding may inform surface synthesis and allow tunable properties and reactivity of nanocrystalline oxides. Analyzing other oxide systems is needed to inform discussion of relevant functional properties of oxide nanopowders and to determine the degree of generality of this effect in oxide nanoparticles. Accordingly, we examine the distribution of oxygen ions in nanoparticles of a dissimilar oxide, yttrium-stabilized cubic zirconium oxide (YSZ), with substantially different properties from those of the aluminum oxide examined previously [11]. YSZ and Al_2O_3 oxides have different crystal lattices and packing, their cationic sublattices contain transition versus non-transition metals, and the values of oxygen diffusion coefficients in these oxides differ by several orders of magnitude [22,23]. Both oxides are used extensively as engineering materials.

Oxygen deficiency in the oxide nanoparticles may be achieved through evaporation of oxygen from the oxide during high-temperature synthesis of nanopowders. Although as mentioned this had been observed and characterized for $\alpha\text{-Al}_2\text{O}_3$ (0001) crystalline surfaces in the $\sqrt{31} \times \sqrt{31}R9^\circ$ reconstruction, the direct evidence for a similar effect in $\gamma\text{-Al}_2\text{O}_3$ nanopowders was quantified by us only recently [11]. No similar reconstructions have been characterized for pure zirconia monocrystals, much less for YSZ samples. In the case of c- ZrO_2 and YSZ, crystalline defects are common and the surfaces challenging to characterize partly due to phase competition and the associated chemical differences with low-percentage addition of other metal oxides to stabilize the cubic phase of zirconia. Nevertheless, a number of studies have characterized the low-index surfaces of zirconia and related oxides in monoclinic, tetragonal, and cubic phase, which may convert to tetragonal in the absence of cubic-stabilizing additions [24–32]. Unlike alumina where single-aluminum termination is favored in the absence of hydrogen [33], DFT with associated thermodynamic and molecular dynamics predictions of crystalline tetragonal or cubic zirconia surfaces show stoichiometric oxygen-terminated (111) surfaces presenting “O-Zr-OO-Zr-O...” layering to be the most stable thermodynamically spanning all relevant oxygen partial pressures [31,34].

Accordingly, in crystalline samples, there is well-characterized evidence for oxygen-deficient surfaces of alumina but not of zirconia or YSZ. Nanopowders uniquely emphasize surface over bulk thermodynamics since more than ten percent of total atomic content can be comprised of surface or near-surface species in these samples, whereas for monocrystals the surface might be considered a “perturbation” of the bulk crystal. In terms of surface energies, the “Al (111)” monolayer over the Al-O₃-Al-Al-O₃-Al... $\alpha\text{-Al}_2\text{O}_3$ (0001) surface may present a lower energy surface, with Al (111) surface energy estimated at $\sim 1000 \text{ mJ m}^{-2}$ [35], while $\alpha\text{-Al}_2\text{O}_3$ (0001) is more than twice that value [36]. Conversely, the estimates for Zr (0001) of close to $2,000 \text{ mJ m}^{-2}$ [37–40] are $\sim 40\%$ higher than for cubic or tetragonal ZrO_2 (111) [24,25,28]. Consequently, simple analysis based on clean surface energy estimates from monocrystals does not provide an explanation for why metal oxide nanopowders might prefer metal-enriched overlayers. Nonetheless, experimental evidence pointing to oxygen deficiency at the surfaces of these samples is fairly ubiquitous.

In this current study, we present direct evidence for oxygen loss from the surface layer of YSZ10 nanopowders. We synthesize a series of nanopowders enriched in ^{18}O with increasing specific surface area. These samples are characterized using X-ray diffraction (XRD). We quantify ^{16}O and ^{18}O content in nanopowders using NRA and analyze oxide oxygen content versus oxygen uptake post-synthesis. We examine the thermal stability of these nanopowder surfaces and, using density functional calculations, explore the impact of oxygen depletion on nanopowder surface and electronic structure.

2. Samples and methods

The nanopowder samples were produced by laser evaporation of a ceramic target. The initial material for preparing the target was commercial micropowder YSZ10 (ZrO_2 –10 mol% Y_2O_3) or $\text{Zr}_{0.82}\text{Y}_{0.18}\text{O}_{2.56}$. XRD analysis identified cubic structure with lattice parameters of 0.5145 nm. The initial pellet compaction was performed in air at room temperature and produced pellets of 15 mm diameter with 10–15 mm thickness and a density 35–40% of the theoretical density. Before preparing the target pellet for laser evaporation, the oxygen sublattice of the initial micropowder was enriched with ^{18}O isotope. For this purpose, the initial powder was annealed for 24 hours at 800 °C and 1 atm oxygen pressure enriched with 80% ^{18}O isotope. The annealing was performed in an alundum tube containing the pellets pressed from the initial powder. After annealing, the NRA results indicated about 15% enrichment in ^{18}O isotope of the oxygen sublattice. The ^{18}O -enriched powder then was ground in a mortar made of zirconium oxide to a powder with a specific surface area of $2.2 \text{ m}^2/\text{g}$. This ^{18}O -enriched micropowder was pressed in air at room temperature to produce a 60 mm diameter target for use in laser evaporation preparation of the nanopowders.

A fiber ytterbium laser with 1 kW maximum power operating at an irradiation wavelength of $1.07 \mu\text{m}$ was used in the nanopowder synthesis. Laser evaporation of the ceramic target was performed in an inert atmosphere (argon or helium) to prevent oxygen isotope exchange during synthesis. We needed to produce samples over a wide range of specific surface area values to characterize behavior for different average particle sizes. Accordingly, the type of inert gas (argon or helium), gas pressure, and laser power were varied and both pulsed and continuous modes of laser irradiation of the target were used during synthesis. In pulsed mode, the pulse duration was 60 μs and the frequency was 5 kHz. Laser radiation was focused on the target using an Optoskand d25 f60/200 optical system, which provided a maximum laser power density on the target surface of 10^7 W/cm^2 . Regular wear of the target during laser irradiation was achieved by rotating the target and by its reciprocating motion in the plane perpendicular to the laser beam axis.

The conditions for nanopowder synthesis, the values of their specific surface area S and average sizes of X-ray coherent scattering domains are listed in Table 1. The specific surface area of the powders was determined using the BET method [41]. According to transmission electron microscopy data, the nanopowders had narrow particle size distribution and contained no particles larger than $1 \mu\text{m}$ since the synthesis apparatus was equipped to remove larger particles. X-ray diffraction (XRD) analysis of the nanopowders was performed using a DISCOVER D8 (Bruker) diffractometer operating at 40 kV and 40 mA with $\text{Cu-K}\alpha$ radiation ($\lambda = 0.1542 \text{ nm}$) equipped with a graphite monochromator on a secondary beam and scintillation detector in the Bragg–Brentano configuration. Bruker software TOPAS-3 with Rietveld full-profile refinement was employed for the quantitative analysis. The average size of coherent diffraction domains (crystallite size) was estimated by using the Scherrer approach with a correction coefficient of 0.89.

The X-ray diffraction spectra in Fig. 1 indicated that all nanopowders and the initial micropowder were monophase with a cubic lattice. The diffraction line width monotonously increased with the specific surface area of the powders. The line shape shows that virtually no amorphous phase and microstresses were in the nanopowders.

In some cases, we used thermogravimetry to estimate the quantity of adsorbed oxygen-containing molecules in the nanopowders. Analysis was carried out on an NETZSCH STA409 thermal analyzer equipped with a quadrupole mass spectrometer. The powders were heated at a rate of 10 K/min while dry argon was passed through the chamber.

The NRA study was performed using a 2-MV Van de Graaff accelerator. In preparation for measuring average concentrations of isotopes ^{16}O and ^{18}O , the YSZ10 micro- and nanoparticles were pressed in an indium plate. Rutherford backscattering spectrometry measurements showed

Table 1
Synthesis modes and parameters of YSZ10 oxide nanopowders.

Synthesis mode	Average power of laser irradiation, W	Gaseous atmosphere during synthesis	Gas pressure during synthesis, Torr	Specific surface area of nanopowder, S , m^2/g	Average size of coherent diffraction domain, nm
Continuous	960	Argon	1450	41	33
Pulsed	68	Argon	760	83	18
Pulsed	95	Helium	670	171	6.5
Pulsed	68	Helium	290	243	4.0

only oxygen, zirconium, and yttrium atoms present in the analysis zone. Indium atoms were lacking because the thickness of the oxide layer ($>1 \mu\text{m}$) on the indium surface was greater than the depth of the analysis zone. In some instances, the powders were pressed in copper powder instead of indium plate. These different substrates did not change the results of the NRA measurements. For measuring the concentration of ^{16}O isotope, the reaction $^{16}\text{O}(\text{d}, \text{p}_1)^{17}\text{O}^*$ with deuteron energy of 900 keV was used, while the concentration of ^{18}O isotope was determined via the reaction $^{18}\text{O}(\text{p}, \alpha)^{15}\text{N}$ with proton energy of 762 keV. The diameter of incident deuteron and proton beams ranged from 0.5 to 1 mm. In our NRA experiments, at least 10^{12} nanopowder particles were in the analysis zone, which allowed correct measurement of the average oxygen isotope concentrations for an ensemble of nanoparticles. Further investigation showed that the nanopowders had inhomogeneous distribution of oxygen ions in the nanoparticles. Concurrently, the shape of the spectra of both nuclear reactions corresponded to samples with constant concentration of ^{16}O and ^{18}O isotopes in the depth. This was related to the nanopowders containing few if any large particles with size exceeding the depth of the NRA zone. By way of example, Fig. 2 depicts several spectra of reaction $^{18}\text{O}(\text{p}, \alpha)^{15}\text{N}$. A silicon surface detector with a diameter of about 10 mm registered nuclear reaction products (protons or α -particles) using an 160° angle of registration. The radiation dose, i.e., the number of incident beam particles falling on the sample, was determined via a secondary monitor with about 0.5% statistical error in those measurements.

For analysis of the nuclear reaction products spectra, we employed a comparison procedure relating the spectra from the YSZ samples with a reference sample having a constant in-depth concentration of oxygen. This procedure allows the concentrations of light element isotopes to be determined within 1% accuracy for depths up to one μm if the concentrations of isotopes in the samples vary inconsiderably with depth [42]. Additionally, it requires neither accurate measurement of nuclear reaction sections nor consideration of different factors leading to spectral broadening. Copper (II) oxide, CuO , was used as the

reference sample in the form of a compacted pellet produced from ultrapure micropowder subjected to long-term annealing in air at 900°C . No significant deviations from CuO stoichiometry were found by Rutherford backscattering spectrometry and NRA. In the mathematical analysis of the spectra, it was assumed that the micropowder and nanopowders of YSZ10 had the composition $\text{Zr}_{0.82}\text{Y}_{0.18}\text{O}_x$, and the values of x and y were then determined. Details of the spectra comparison procedure and analysis used to obtain oxygen indices x and y are provided in Supplementary Material.

When the values of oxygen indices x and y are determined, systematic errors may arise from use of experimental data on stopping powers [43], the additive Bragg rule [44], and other factors. The degree of such errors may be estimated by obtaining linear dependences of the oxygen indices on the specific surface area of nanopowders, $x(S)$ and $y(S)$, and extrapolating these to $S = 0$. As shown previously [11], such dependences indicate oxygen deficiency or oxygen excess is localized in the thin near-surface layer of nanoparticles. After synthesis, all nanopowders were kept under the same ambient conditions so $x(S = 0)$ and $y(S = 0)$ can be interpreted as the values of oxygen indices for the crystal lattice of YSZ10. In this study, we found $x(S = 0) + y(S = 0) = 1.93 \pm 0.05$. According to the electro-neutrality condition, YSZ10 has the composition $\text{Zr}_{0.82}\text{Y}_{0.18}\text{O}_{1.91}$, in agreement with the value found from the NRA version employed here and indicating no notable systematic errors in determining the values of indices x and y .

To further investigate the impact of surface oxygen deficiency in metal oxide nanopowders, we performed density functional calculations on model c-ZrO_2 surfaces progressively depleted of oxygen to achieve zirconium-terminated surfaces to the depth of oxygen depletion suggested from our NRA results. The calculated cubic bulk unit cell had Fm-3m symmetry with $5.07 \text{ \AA}$ lattice vectors. The periodic surface cells maintained $>10 \text{ \AA}$ (eight or more layers) of the regular

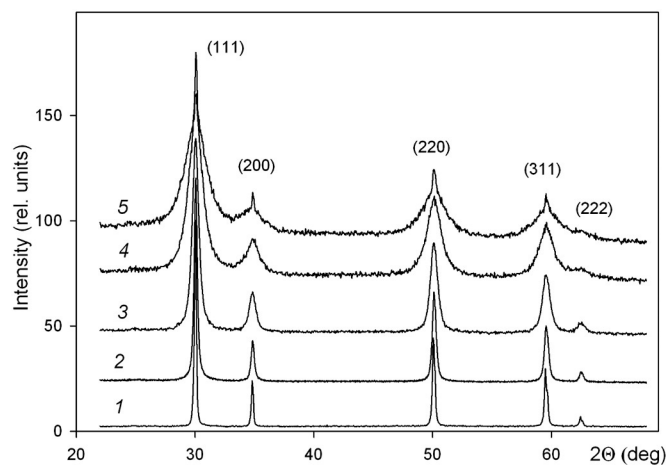


Fig. 1. The XRD spectra for YSZ10 with 1, 2, 3, 4, and 5 denoting spectra for the micropowder and nanopowders with the specific surface area 2.2, 41, 83, 171, and $243 \text{ m}^2/\text{g}$, respectively.

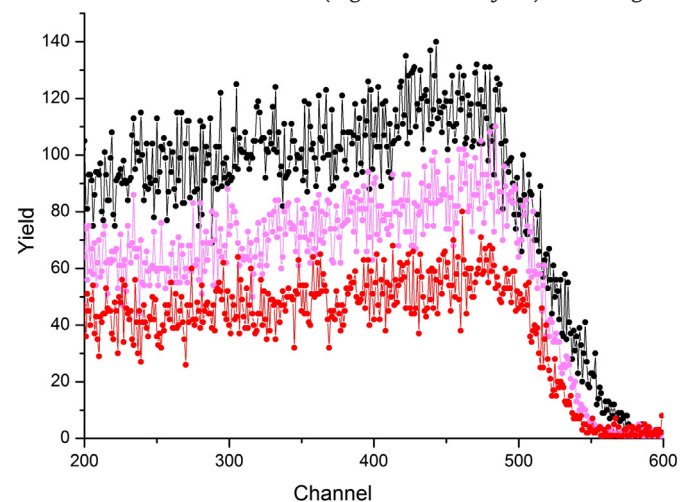


Fig. 2. The spectra of nuclear reaction products $^{18}\text{O}(\text{p}, \alpha)^{15}\text{N}$ obtained at equal radiation dose of samples: black—micropowder, lilac—nanopowder with specific surface area $S = 83 \text{ m}^2/\text{g}$, and red—nanopowder with specific surface area $S = 243 \text{ m}^2/\text{g}$. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

oxygen lattice separating the equivalent zirconium-enriched surfaces which were separated by at least 10 Å of vacuum normal to the surface. The Perdew–Burke–Ernzerhof non-local gradient-corrected exchange functional was used to calculate the exchange–correlation energy and potential [45]. All calculations employed Monkhorst–Pack grids resulting in a k-point mesh of 0.05 Å^{-1} or finer spacing and a plane wave basis cutoff of 340 eV for the valence electron density with ultra-soft pseudopotentials [46] used to describe ion–electron interactions as implemented in CASTEP [47]. All calculations required convergence within 1.0×10^{-6} eV/atom for the SCF cycles and for the optimization of ionic coordinates within 5.0×10^{-5} eV/atom energy change, 0.05 eV/Å maximum force, and 5.0×10^{-3} Å maximum displacement between cycles.

The low index (111), (100), and (101) surfaces of c-ZrO₂ were studied with surface zirconium enrichment through oxygen loss of up to two stoichiometric oxygen layers nearest to the surface, analogous to that observed in the α -Al₂O₃ (0001) surface reconstruction and suggested as the maximum loss estimated by our NRA analysis. Given the XRD results in Fig. 1 and that the (111) surface is calculated to be the most thermodynamically favorable, we focused our subsequent analyses exclusively on this surface. (The structures of these analyzed surfaces are available in Supplementary Material.) Density functional calculations are performed on periodic surface cells derived from a c-ZrO₂ unit cell without yttria since our interest was in oxygen-depleted surfaces and only near subsurface layers are represented in periodic slab models with too few unique atoms to accommodate low-percentage dopants. Previous studies have found surface and near-surface yttrium content unnecessary for reconciling computed and experimental surface results in certain low-index terminations [27,28].

3. Results and discussion

Fig. 2 displays selected spectra of nuclear reaction products $^{18}\text{O}(\text{p},\alpha)^{15}\text{N}$ obtained at equal radiation dose of samples. The yield, corresponding to the average concentration of ^{18}O isotope, decreases significantly as the specific surface area of the powders increases. At the same time, the spectra of nuclear reaction products $^{16}\text{O}(\text{d},\text{p}_1)^{17}\text{O}^*$ for the powders characterized by different specific surface areas show insignificant differences from each other. Analogous data were obtained in work [11] for Al₂O₃ powders.

Results and analysis of spectra of the nuclear reaction products $^{18}\text{O}(\text{p},\alpha)^{15}\text{N}$ and $^{16}\text{O}(\text{d},\text{p}_1)^{17}\text{O}^*$ presented in Table 2 and Fig. 3 indicate that oxygen depletion from the oxide followed by subsequent uptake of ambient oxygen takes place during high-temperature synthesis, cooling, and storage of nanoparticles. During nanopowder synthesis, ^{18}O atoms are evaporated from a thin surface layer of the nanoparticles. The thickness of this layer does not depend on the size of nanoparticles. This is seen by the reduction of the oxygen index $y(S)$ with an increase in the specific surface area S and by the linear dependence of $y(S)$. It is reasonable to assume equal fractions of ^{16}O and ^{18}O atoms evaporated from the nanopowders during synthesis. It follows that high-temperature synthesis using laser evaporation produces surfaces with substantial oxygen deficiency in the nanoparticles compared with stoichiometric Zr_{0.82}Y_{0.18}O_{1.91}. Post-synthesis, all nanopowders were kept under identical conditions for cooling and storage. The values of ^{16}O content $x(S)$ contrasted with the decreasing fraction of ^{18}O

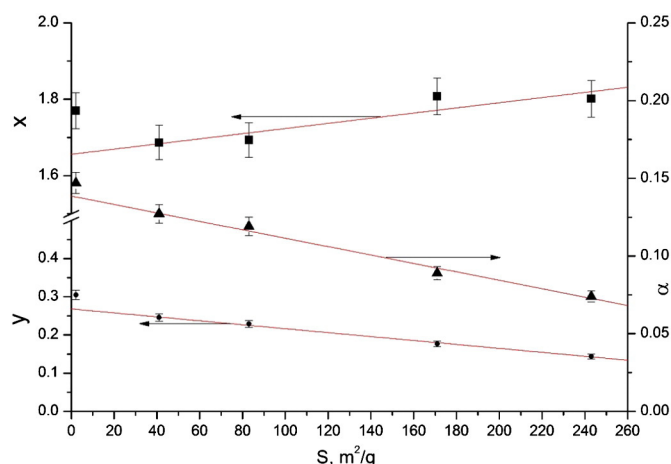


Fig. 3. The dependence of oxygen indices x (squares), y (dots), and the degree of enrichment of the oxygen sublattice α (triangles) with ^{18}O isotope on the specific surface area of powders S for the micropowder and nanopowders of Zr_{0.82}Y_{0.18}O_x oxides. The linear approximations $x(S)$, $y(S)$, and $\alpha(S)$ are given with consideration of the data only for the nanopowders.

relative to total oxygen content $\alpha(S)$ in Table 2 and the linear dependences of these values with respect to specific surface area in Fig. 3 indicate additional ^{16}O atoms join the depleted surface region of the nanoparticles. As in the case of evaporation of ^{18}O , the thickness of this layer did not depend on the size of nanoparticles. The uptake of ^{16}O atoms in the nanopowders upon cooling and storage under ambient conditions could include oxidation processes as well as chemisorption and physisorption of oxygen-containing molecules, including water.

The loss of oxygen atoms from the surface region of nanoparticles at high temperature may be due to a discrete mechanism of evaporation of near-surface oxygen atoms from the oxides. This is supported by our previous studies for α - and γ -Al₂O₃ [11,19] achieving surfaces similar to the $\sqrt{31} \times \sqrt{31} \text{ R}9^\circ$ reconstruction. At high temperature, the outermost oxygen layer(s) in these samples leaves the oxide to create a metal-enhanced surface; oxygen deficiency in the oxide then persists well beyond conditions where this surface termination is favored thermodynamically. Following this idea, one can derive the following expression for the relative concentration of oxygen atoms in spherically shaped nanoparticles:

$$\frac{N}{N_{\text{st}}} = 1 - 3k \frac{d}{R}, \quad (1)$$

where N and N_{st} are the number of oxygen atoms in equal volumes of crystal lattices for nanoparticles and for stoichiometric oxide; $k = 1, 2$ is the number of oxide layers, from which oxygen atoms evaporate during high-temperature synthesis; d is the thickness of the oxide layer, depleted of oxygen atoms through evaporation during high-temperature synthesis; and R is the average radius of oxide nanoparticle. Equation (1) assumes that $d \ll R$ and homogeneous distribution of oxygen ions in the oxide. The value of d is assumed to be equal to the minimal distance between comparable oxygen ions in the oxide, and the nanoparticle radii R are calculated using $R = 3/\rho S$, where ρ is the oxide density. This expression supposes that all nanoparticles in a specific surface area characterized sample have equal radius.

According to Eq. (1), a universal linear dependence $\frac{N}{N_{\text{st}}} \left(\frac{d}{R} \right)$ for all oxide nanopowders may occur if the oxygen atoms evaporate from an equal number of oxide layers during nanopowder synthesis. Fig. 4 shows that these dependences are close to each other for aluminum oxide and YSZ10 nanopowders. For aluminum oxide, we analyze values obtained from our previous work [11], and for YSZ10, we employ the values from this study shown in Table 2. For plotting the dependences in Fig. 4, the values of density ρ are assumed to be

Table 2

Parameters of Zr_{0.82}Y_{0.18}O_x powders after synthesis, cooling, and ambient storage.

Specific surface area S , m ² /g	x	y	$\alpha = \frac{y}{x+y}$
2.2	1.77 ± 0.05	0.30 ± 0.01	0.147 ± 0.007
41	1.69 ± 0.05	0.25 ± 0.010	0.127 ± 0.006
83	1.69 ± 0.05	0.229 ± 0.009	0.119 ± 0.005
171	1.81 ± 0.05	0.177 ± 0.007	0.089 ± 0.004
243	1.80 ± 0.05	0.144 ± 0.006	0.074 ± 0.004

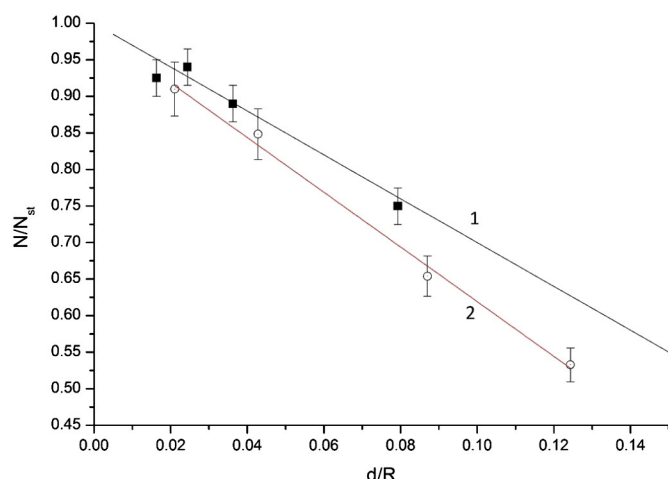


Fig. 4. The average relative concentration $\frac{N}{N_{st}}$ versus the average distance between oxygen ions in oxide d and the average nanoparticle radius R : squares—the experimental data for aluminum oxide borrowed from work [11]; circles and line 2—the experimental data obtained in this study for YSZ10; 1—the calculation by expression (1) at $k = 1$.

3.70 and 5.92 g/cm³ for aluminum oxide and YSZ10, respectively. For aluminum oxide, the dependences $\frac{N}{N_{st}}(\frac{d}{R})$ coincide with experimental error for $k = 1$. For YSZ10, the slope ratio in the linear dependence $\frac{N}{N_{st}}(\frac{d}{R})$ of 3.8 ± 0.2 is noticeably greater than the theoretical value of 3; specifically, this discrepancy was 11% at the root-mean-square measurement error of about 4%.

This analysis of our results is derived with the use of simple approximations, including spherical nanoparticle shape and homogeneous distribution of oxygen atoms in the crystal lattice of oxides. In the evaporation process described by expression (1), the crystal structure of the nanoparticles is not taken in to account. Of course, when DFT is used to investigate our surface models, the evaporation of oxygen atoms from definite crystallographic planes is considered. Thus, it may not be meaningful to quantitatively analyze the $\frac{N}{N_{st}}$ values for YSZ10 beyond noting that evaporation of somewhat more than one O₂ “layer” is suggested—the ideal surface termination O-Zr-OO-Zr-OO-... becoming Zr-O-Zr-OO-, Zr-Zr-OO-, or possibly Zr-Zr-O-... The data in Fig. 4 indicate similar surface oxygen depletion mechanisms impact the dissimilar oxides of aluminum oxide and YSZ10 at high temperatures resulting in an overlayer enriched in metal on the surface.

In the Al₂O₃ nanoparticles, evaporation of the near-surface oxygen results in a metal overlayer similar to the $\sqrt{31} \times \sqrt{31}R^9$ reconstruction on α -Al₂O₃ (0001). That reconstruction in α -Al₂O₃ is anticipated to require loss of two “layers of oxygen” (O₃ units) to result in sufficient aluminum surface content to rearrange to a nominally Al (111) surface [17,19]. Due to significant relaxations of this surface aluminum, the thickness of this resulting overlayer is effectively a layer of aluminum over an Al₂O₃ sublayer terminated by the thermodynamically favored Al-termination. Lower symmetry and increased defects in other alumina phases means that the detailed surfaces and reconstructions of those are not as well characterized.

Unlike aluminum oxide where an oxygen-deficient surface reconstruction is well characterized, the precise atomic structure in zirconia is not well understood due to competing phases, surface energy trends in the metal versus oxide, and inclusion of yttria or other stabilizing metal content as described earlier. As mentioned, the single O termination (O-Zr-OO-Zr-OO-...) of zirconia in the absence of hydrogen is thermodynamically favored for clean surfaces. Achieving an A-B overlayer of the A-B-A-B hcp Zr (0001) surface (Zr-Zr-O-Zr-OO-Zr-...) also requires loss of two O₂ units of oxygen in the ZrO₂ (111) surface cell, while achieving a monolayer of Zr with nearest subsurface neighbors partially coordinated with oxygen from below (Zr-Zr-OO-Zr-...) only

requires loss of 1.5 O₂. Our experimental analysis suggests that, by completion of high-temperature synthesis, nanoparticle nuclei have stoichiometric composition with an oxygen-deficient surface layer d of slightly over 3 Å thickness, coinciding with the later model. The NRA results do not allow us to assert that the outer layer of oxide nanoparticles consists *only* of metal atoms or make definite conclusions about the character of bonding, i.e., ionic, covalent, or metallic, between atoms in the outer atomic layer of nanoparticles. Nevertheless, our DFT calculations display dramatic surface electronic structure impact over a broad range of oxygen depletion values suggested by the thickness derived from our NRA results. Fig. 5 shows loss of a single, 1.5 or two O₂ unit(s) from the (1 × 1) periodic surface (Fig. 5c–e, respectively) creates surface states closer in electronic structure to metallic Zr (Fig. 5f) than to those of the metal oxide (Fig. 5a). Accordingly, regardless of the detailed structure of the depleted surfaces, this effect should have substantial impact on the surface electronic states and subsequent reactivity.

Our current oxygen-depleted surface models for zirconia indicate metallic surface states with limited oxygen loss. High-resolution transmission electron microscopy (HRTEM) studies of nanocrystalline Yb₂O₃-ZrO₂ display metal positions as the bright content with little sensitivity to particular metal or dark oxygen content [48]. As can be seen in Fig. 6, Zr positions in hexagonal Zr (0001), the most stable face and structure of pure zirconium metal, effectively coincide with those of the zirconium-enriched ZrO₂ surfaces achieved upon oxygen depletion in our DFT calculations. The in-plane lattice vectors from our bulk ZrO₂ are expanded by 4% relative to the pure metal, and this matching will vary slightly depending on the element and percentage content of metals added to stabilize the cubic zirconia phase. The broad features of oxygen-deficient surfaces being difficult to distinguish in HRTEM images but having notable surface electronic structure impact should apply regardless of particular metal added for phase stabilization or precise extent of the oxygen depletion.

For fundamental as well as practical understanding, it is important to determine the thermal stability of oxygen deficiency in nanoparticles. The data of Table 2 qualitatively display oxygen deficiency not only at the nanoparticle synthesis temperature but also at room temperature. This initially may not be obvious from the numerical values shown. However, if the crystal lattice of nanoparticles had stoichiometric composition as well as adsorbed surface oxygen, the oxygen index x should grow as nanopowder specific surface area increased since adsorbed oxygen-containing molecules present on the surface of nanoparticles would increase as well. The values in Table 2 indicate that this does not occur but leaves the quantity and nature of adsorbed species ambiguous.

To quantify and better understand the trend in ¹⁶O, we performed NRA measurements of the concentration of ¹⁶O isotope in the nanopowder with specific surface area $S = 243$ m²/g at elevated temperature. The powder was heated up to 400 °C in vacuum using a resistance furnace immediately during measurement of the concentration of ¹⁶O isotope. Such temperature is usually sufficient for removing adsorbed water molecules and other gases (as also noted recently in spectroscopy studies of stabilized zirconia nanoparticles [49]), but it is not sufficient for removing chemisorbed molecules or for thermal decomposition of oxides. In our experiments, the pressure in the chamber of the accelerating installation was below 10^{−6} Torr. During isothermal exposure at 400 °C for 70 min, the oxygen index x in Zr_{0.82}Y_{0.18}O_x¹⁶O_{0.144} oxide decreased. The value of index x obtained in 70 min is given in column 3 of Table 3; further exposure in vacuum at 400 °C did not change this value appreciably. Columns 1 and 2 of Table 3 also list the values of x in the same nanopowder, which are mentioned earlier and in Table 2.

Thermogravimetry studies displayed analogous results pointing to removal of oxygen-containing molecules from the nanopowder with specific surface area $S = 243$ m²/g. For these, the powder was heated with a rate of 10 K/min, dry argon was passed through the chamber,

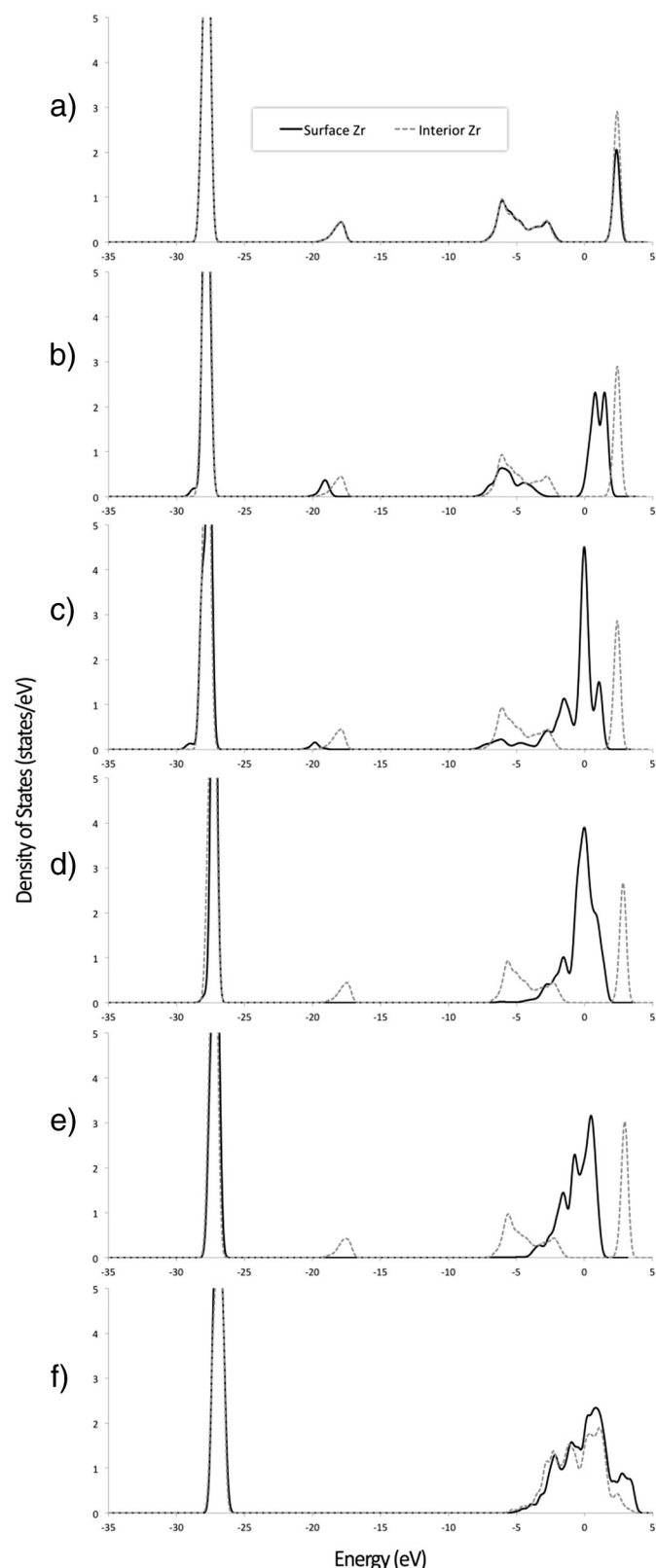


Fig. 5. Density of states projected onto zirconium atoms at the surface (solid line) and in the interior (dashed line) of (a) initially stoichiometric c-ZrO₂ (111), (b) ZrO₂ with removal of outermost oxygen, (c) ZrO₂ with two nearest surface oxygen removed, equivalent to one stoichiometric oxygen removal, (d) ZrO₂ with three nearest surface oxygen removed, (e) ZrO₂ with four nearest surface oxygen removed, and (f) Zr (0001). The Fermi level is set to zero in the states where metallic DOS exist and the core levels are aligned for surface and interior atoms. Loss of oxygen from the ZrO₂ surface results in surface states similar to those of pure zirconium metal.

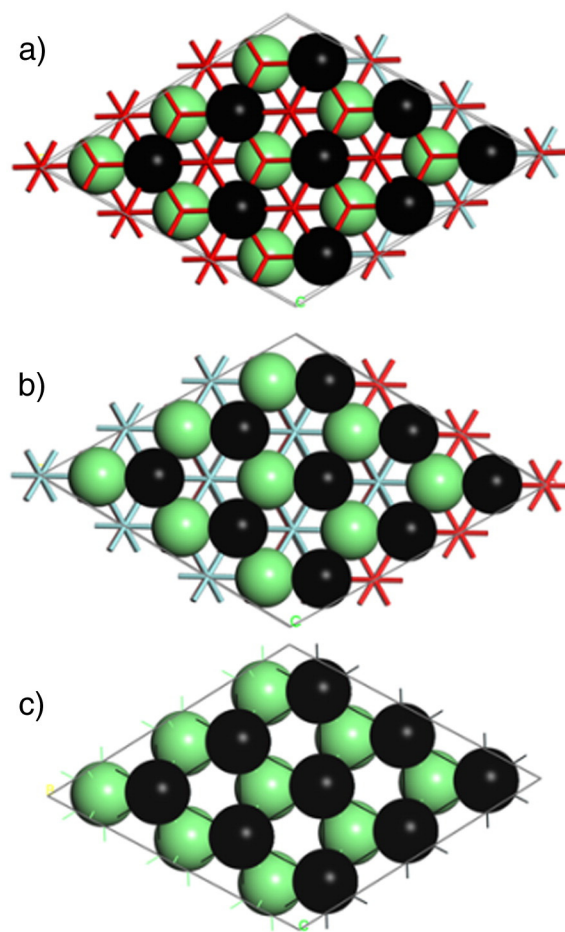


Fig. 6. Top view of supercells showing similar structure of the top (black) and second (green) layers of zirconium positions in (a) the 2×2 stoichiometric c-ZrO₂ (111) surface, (b) the 2×2 depleted oxygen surface with two stoichiometric layers of oxygen removed, and (c) on the 3×3 pure Zr (0001) surface. Additional atomic positions of red O and subsurface blue Zr are indicated by the stick vertices.

and using a mass spectrometer, we registered that only H₂O and CO₂ molecules are removed from the powder. The quantity of H₂O molecules was much greater than the quantity of CO₂ molecules. The change in the mass of the powder occurred mainly during its heating up to 500 °C; the mass loss of the nanopowder was 12.27%. Column 4 of Table 3 exhibits the results of thermogravimetric experiments. The value of index x in column 4 is obtained in the approximation that the mass loss 12.27% is due to desorption of only H₂O molecules.

The data of Table 3 show that oxygen deficiency in the crystal lattice of YSZ10 nanoparticles is practically the same at the temperature of synthesis and at room temperature. The differences in the values of x in column 1 of Table 3 versus and in columns 3 and 4 are minimal. They can be due to the employed methods. For example, during annealing of nanopowders in vacuum and in dry argon, kinetic limitations could cause incomplete removal of adsorbed oxygen-containing molecules. Thus, according to our measurements, the crystal nanoparticles of YSZ10 have almost identical structure and composition. Their nucleus has the stoichiometric composition Zr_{0.82}Y_{0.18}O_{1.91}, and the outer atomic layer contains no or very limited oxygen content. At the same time, the nanoparticles at room temperature differed from those at the temperature of synthesis by having a large number of adsorbed oxygen-containing molecules, mainly H₂O, on the surface. Note that in this study, the results are obtained with the use of the high-temperature technology of laser sputtering of a ceramic target for synthesis of nanoparticles. Perhaps, our results are also valid for other high-temperature technologies for synthesis of nanopowders

Table 3The values of oxygen index x for $Zr_{0.82}Y_{0.18}O_x$ $^{18}O_{0.144}$ oxide nanopowder with specific surface area $S = 243 \text{ m}^2/\text{g}$.

Calculated value according to NRA data, by completion of high-temperature synthesis	Experimental value according to NRA data, after cooling and storing of the powder (as in Table 2)	Experimental value according to NRA data, after vacuum annealing at 400 °C	Calculated value according to thermogravimetric data
1 0.89 ± 0.03	2 1.80 ± 0.05	3 1.00 ± 0.03	4 0.97 ± 0.03

in which oxygen atoms can evaporate from the outer atomic layer of nanoparticles, but we have not explored other preparation methods.

The number of atoms in the surface of the nanopowders comprises a large fraction of the overall number of atoms in the nanocrystal. Accordingly, nanopowders may not exhibit surface structures and content anticipated for bulk oxides. Electric field tuning has been shown to permit some control of oxygen stoichiometry in thin film zirconia surfaces [50]. We show that high-temperature synthesis using laser evaporation results in oxygen-deficient surfaces for varied metal oxide nanopowders, indicating that careful attention to nanopowder synthesis and storage conditions may achieve surface structure and stoichiometry that would not be predicted thermodynamically for monocrystals. Heterogeneous catalysis applications require precise surface electronic structure and reactivity; the possibility of tuning 2D metallic surface states of metal oxide nanoparticles that appear to be nonmetallic [51] may permit new control and deeper insight into the complex mechanisms of these reactions. Exploiting the oxygen depletion effect in metal oxide nanopowder synthesis remains an important area for future studies and refinement.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <http://dx.doi.org/10.1016/j.susc.2015.10.011>.

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