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SYNTHESIS AND PROPERTIES OF INORGANIC COMPOUNDS

Oxygen Nonstoichiometry of Nanocrystalline Ceria

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Abstract—Correlation relations between oxygen nonstoichiometry and particle size in nanocrystalline CeO_{2-x} are revised. The ceria unit cell parameter is shown to increase from 0.5410 to 0.5453 nm as the particle size decreases from 23 to 2.3 nm. The CeO_{2-x} critical particle size where cerium(IV) is completely reduced to cerium(III) is calculated as 1.1–1.3 nm.

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Nanocrystalline ceria is a multifunctional material having a wide spectrum of applications on account of the unique complex of physicochemical properties including a well-defined dependence of key parameters, such as oxygen nonstoichiometry as well as optical and electrophysical properties, on the CeO_{2-x} particle size.

The first piece of evidence for the dependence of the oxygen nonstoichiometry and unit cell parameter on the particle-size in CeO_{2-x} was obtained by Tsunekawa et al. [1–4] in studying virtually monodisperse ceria particles having sizes of 6.7, 3.8, and 2.1 nm. The unit cell parameter for these particles was determined as 0.5453, 0.5488, and 0.5560 nm, respectively, and their bulk composition was respectively formulated as $CeO_{1.894}$, $CeO_{1.810}$, and $CeO_{1.630}$ [1], whereas for coarse-grained ceria, the unit cell parameter is 0.5411 nm.

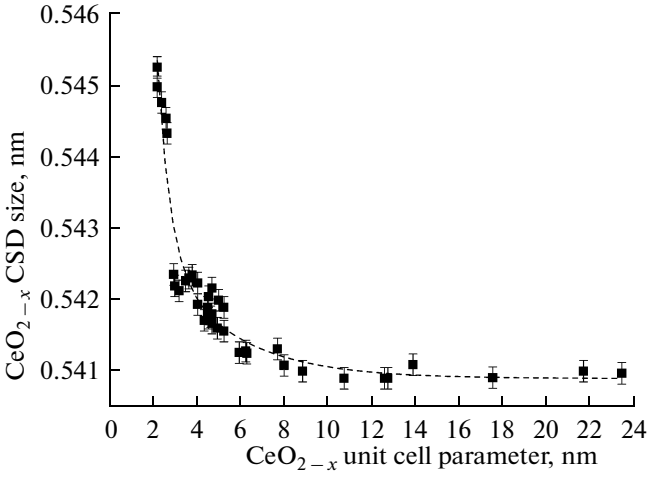
Wu et al. [5] analyzed the composition of CeO_{2-x} nanoparticles 3–20 nm in size prepared by a gas-phase method. They determined that the unit cell parameter varies within 0.541–0.561 nm as a function of particle size; thus, their determined variation range of the unit cell parameter slightly exceeded the one indicated by Tsunekawa et al. [1–4]. Wu et al. [5] were of opinion that this discrepancy stems from greater nonequilibrium in CeO_{2-x} nanoparticles preparation. Electron energy loss spectroscopy showed that the oxygen nonstoichiometry of nanoparticles is enhanced from the center to periphery. Thus, ceria nanoparticles are actually core/shell nanostructures; in relatively large particles, cores represent near-stoichiometric ceria and the surface composition approaches Ce_2O_3.

For CeO_{2-x} particles with sizes of 6.1–80 nm prepared by homogeneous precipitation from cerium(III) nitrate in the presence of hexamethylenetetramine, Zhang et al. [6] found that the unit cell parameter ranged from 0.543 to 0.541 nm. Noteworthy, both the values themselves and their range are smaller than indicated in [1–5]. Zec et al. [7] obtained similar results: the unit cell parameter of CeO_{2-x} particles with sizes of 6.2–8.5 nm synthesized in inverted microemulsions was 5.409–5.403 nm. Values reported for the critical CeO_{2-x} particle sizes where the effective oxidation number of cerium becomes +3 found in various sources are also noticeably divergent: 1.5 nm in [1] against 3 nm in [5].

According to Tsunekawa et al. [4, 8], the aforementioned distinctions can arise from the different shapes of differently prepared CeO_{2-x} nanoparticles: unit cell parameter versus particle size plots having greater slopes are observed for spherical or ellipsoidal particles, whereas particles with octahedral faceting typically have plots with smaller slopes. However, the existing body of relevant experimental data is not large, and this suggestion is quite disputable. Therefore, this work details the influence of size factor on the oxygen nonstoichiometry of ceria nanoparticles having various chemical histories and synthesized using various methods of soft chemistry.

EXPERIMENTAL

The rapid precipitation of nanodisperse ceria [9, 10] was performed as follows. Aqueous and aqueous–isopropanolic solutions of $(NH_4)_2Ce(NO_3)_6$ and $Ce(NO_3)_3 \cdot 6H_2O$ (0.02, 0.08, 0.3, and 0.8 mol/L) where the water/isopropanol (vol/vol) ratio was 1 : 0, 1 : 1, and 1 : 19, were rapidly added with vigorous stirring to aqueous ammonia (3 mol/L) taken in a fivefold molar excess and kept on a magnetic stirrer for 2–24 h at room temperature. Precipitates were washed with



Unit cell parameter vs. particle size in nanocrystalline ceria.

water three times, centrifuged, and dried at 50°C for 12 h.

The cryochemical synthesis of nanodisperse ceria was as follows: The precipitate produced by mixing an aqueous cerium(III) nitrate solution (0.08 mol/L) with aqueous ammonia (3 mol/L) was freeze dried. An aqueous suspension of CeO_2 was sprayed, with vigorous stirring, into a Dewar flask filled with liquid nitrogen; the resulting cryogranules were placed on metallic trays in a Labconco FreeZone 7948030 freeze drier, which was then evacuated to 1 kPa residual pressure. Freeze drying lasted 48 h; the temperature in the chamber was raised slowly from −30 to +30°C.

The homogeneous precipitation of ceria was performed by mixing aqueous solutions of cerium(III) nitrate and hexamethylenetetramine [11, 12] in ratios of 1 : 10 and 1 : 20 (mol/mol) followed by thermostating at 60°C. The cerium(III) nitrate concentration in the initial solutions was 0.00586 mol/L.

Thermal, hydrothermal, and microwave–hydrothermal treatments were used to additionally vary the micromorphology of CeO_{2-x} particles. The hydrothermal and microwave–hydrothermal treatments of ceria slurries prepared by the rapid precipitation of cerium(III) nitrate by aqueous ammonia were carried out at 120, 150, 180, and 210°C for 3 h in a neutral medium. The products were recovered by centrifugation, repeatedly washed with distilled water, and then dried for 2 h in air at 60°C. The thermal annealing of the samples prepared by rapid precipitation or cryochemically was carried out in an SNOL muffle furnace at 200, 300, 400, 500, 600, and 700°C for 2 h.

Microstructure was observed using transmission electron microscopy (TEM) on a Leo912 AB Omega electron microscope using an accelerating voltage of 100 kV (magnifications up to ×500000).

Powder X-ray diffraction analysis was carried out on a Rigaku D/MAX 2500 diffractometer (CuK_α radiation); the goniometer rotation speed was 2°2θ/min. Diffraction peaks were identified with reference to the JCPDS database. Coherent scattering domain (CSD) sizes for ceria samples calculated using the Scherrer relationship

$$D_{hkl} = \frac{K\lambda}{\beta_{hkl}(2\theta)\cos(\theta_0)}, \quad (1)$$

where θ_0 is the peak position; λ is the CuK_α radiation wavelength, equal to 0.154056 nm; and $\beta_{hkl}(2\theta)$ is the true physical broadening of the diffraction peak. The Scherrer constant (K) was set equal to unity.

Physical broadening was calculated from

$$\beta_{hkl} = \beta - s, \quad (2)$$

where β is the full width at half-height of the X-ray diffraction peak and s is instrumental broadening (0.09° ± 0.01°2θ). The contribution from microstrains to peak broadening was ignored. A sapphire single crystal was used as a reference to determine instrumental broadening.

The β value minus background was determined by fitting (111) and (200) peak profiles to the Voigt pseudo-function within 20°–40°2θ:

$$V(\theta) = \frac{2cA}{\pi}\left[\frac{\omega_L}{4(\theta-\theta_0)^2+\omega_L^2}\right] + \frac{2(1-c)A}{\omega_G}\sqrt{\frac{\ln 2}{\pi}}\exp\left[-\frac{4\ln 2(\theta-\theta_0)^2}{\omega_G^2}\right]. \quad (3)$$

Here, ω_L and ω_G are, respectively, the Lorentzian and Gaussian parameters ($\omega_L = \omega_G = \beta$), A is the scaling factor, and c is the relative contribution of the Lorentzian function to the overall reflection intensity.

The D_{hkl} values calculated from $\beta_{111}(2\theta)$ and $\beta_{200}(2\theta)$ differed by no more than 0.2 nm. The arithmetic mean between D_{111} and D_{200} was used as the CSD size (crystallite size).

The Rietveld refinement of the unit cell parameters for ceria samples used JANA2000 software [13]. Peak profiles were fitted to Voigt pseudo-functions in the range 15°–90°2θ including the unmonochromaticity of $CuK_{\alpha1}$ and $CuK_{\alpha2}$ radiations. Background lines were fitted to 15-order Chebyshev polynomials.

RESULTS AND DISCUSSION

Powder X-ray diffraction (PDF 34-394) identified the products prepared by either of the above-described synthesis procedures as single-phase ceria. Examination of (111) and (200) diffraction peak broadening showed that the powders were nanocrystalline; the CeO_{2-x} CSD sizes increase with increasing synthesis temperature and duration (see also [10]). CSD sizes for our CeO_{2-x} test samples ranged from 2.3 to 23 nm. Transmission electron microscopy showed that CeO_{2-x} samples formed directly by the rapid mixing of cerium(III) and cerium(IV) solutions with aqueous ammonia have rather narrow particle size distribu-

tions, whereas annealing of the same samples at temperatures above 400–500°C or their hydrothermal treatment yielded polydisperse powders.

The figure displays a common unit cell parameter a versus particle size plot for all CeO_{2-x} samples we prepared. We may state that all datapoints fall on one curve, where a varies from 0.5410 to 0.5453 nm. The unit cell parameter change (Δa) as a function of particle size (D) is well fitted to the exponential relation

$$\Delta a\ (\text{nm}) = 0.026 D^{-2.2}. \quad (4)$$

Thus, the variation range of the CeO_{2-x} unit cell parameter determined in this work is appreciably narrower than reported in [1–5] and well agrees with data in [6]. The exponent value in Eq. (4) noticeably exceeds similar values reported in [4, 14]. Noteworthy, the Δa values determined for CeO_{2-x} samples having similar particle sizes but prepared using different methods are virtually alike; in other words, variations in parameters of the soft chemical synthesis of nanocrystalline ceria do not influence the oxygen nonstoichiometry of the product, and the CeO_{2-x} particle size remains the only decisive parameter in this context.

In view of the Tsunekawa et al.'s suggestion [1] that nanocrystalline cerium(III) oxide can exist as a C-type cubic phase having a unit cell parameter of ~0.561 nm and CeO_2 and Ce_2O_3 phases are completely miscible, the composition of CeO_{2-x} nanoparticles we synthesized may be determined according to Vegard's rule. In particular, for the samples with the highest dispersion (D = 2.3–2.7 nm), the composition corresponds to formula units $CeO_{1.89}$–$CeO_{1.92}$. Similar estimations performed for ceria doped by tervalent cations (in our case, Ce^{3+}) using the Kim's empirical equation [7, 15],

$$a\ (\text{nm}) = 0.5413 + 0.04612x, \quad (5)$$

for the same samples give a similar range of compositions ($CeO_{1.91}$–$CeO_{1.93}$).

The unit cell parameter a versus particle size relationship (4) allows the critical size to be determined where all cerium ions in ceria become formally three-charged. When the unit cell parameter of C-type cubic Ce_2O_3 [1] is substituted to the aforementioned relationship, the critical size is ~1.1 nm. In turn, according to Wu et al. [5], cerium sesquioxide formed as a result of decreasing CeO_{2-x} particle size has the fluorite structure with two disordered oxygen vacancies per unit cell whose parameter is ~0.556 nm. Similar calculations of the critical particle size using this value give a value of ~1.3 nm for a. The adequacy of our estimates of the critical particle size are additionally verified by the fact that the aforementioned values approximate the doubled unit cell parameter of CeO_{2-x}; that is, in order for cerium(IV) to completely reduce to cerium(III), it is necessary that all CeO_{2-x} unit cells lie on the surface.

In summary, on the basis of analysis of a wide range of samples prepared by soft chemistry, in this work we have revised correlation relations for the dependence of the oxygen nonstoichiometry and unit cell parameter of CeO_{2-x} on its particle size. The CeO_{2-x} critical particle size where cerium(IV) is completely reduced to cerium(III) has been calculated as 1.1–1.3 nm.

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