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Defect and transport properties of nanocrystalline CeO_{2-x}

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Y.-M. Chiang, E. B. Lavik, I. Kosacki, H. L. Tuller, and J. Y. Ying



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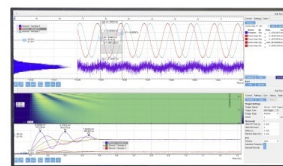
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Defect and transport properties of nanocrystalline CeO_{2-x}

Y.-M. Chiang,^{a),b)} E. B. Lavik,^{a)} I. Kosacki,^{a),c)} H. L. Tuller,^{a)} and J. Y. Ying,^{d)}
Massachusetts Institute of Technology, Cambridge Massachusetts 02139

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It is shown that unique defect thermodynamics and transport properties result for oxides of a few nanometers crystallite size. Fully-dense CeO_{2-x} polycrystals of ~ 10 nm grain size were synthesized, and their electrical properties compared with those of samples coarsened from the same material. The nanocrystals showed reduced grain boundary resistance, 10^4 higher electronic conductivity, and less than one-half the heat of reduction of its coarse-grained counterpart. These properties are attributed to a dominant role of interfacial defect formation. © 1996 American Institute of Physics. [S0003-6951(96)03728-X]

Ultrafine polycrystals of 1–20 nm grain size have received much attention as materials with possibly unique structure and physical properties.¹ For nanocrystalline oxides, potential applications include superplastic forming,² catalysis,³ and gas or electrochemical sensing. Fundamental defect and transport properties govern these properties. The objective of this study was to determine unambiguously any uniqueness of nanocrystalline oxides in this regard. We selected ceria due to its interesting catalytic properties³ and because it is a classical small-polaron electron conductor⁴ with an electron mean-free-path on the order of an atomic separation. Therefore the carrier mobility is not determined by scattering from interfaces, unlike nanocrystalline metals or semiconductors, and allows point defect concentrations to be determined from the absolute electrical conductivity.

Fully dense CeO_{2-x} nanocrystals were pressure-densified (1.1 GPa, 600 °C) from powders of ~ 5 nm particle size prepared by inert-gas-condensation (designated IGC)^{1,5} and thermal decomposition of freeze-dried cerium acetate (designated CP). The densified nanocrystals have ~ 10 nm average grain size (Fig. 1), and as such are amongst the finest-grained ceramics ever prepared in bulk form. Lattice fringes are observed meeting at atomically abrupt grain boundaries with no apparent amorphous grain boundary phase. Coarse-grained comparison samples of $\sim 5 \mu\text{m}$ grain size were prepared by firing nanocrystalline samples at 1200 °C for 12–15 h.

Bulk and interfacial contributions to the total electrical conductivity were separated using impedance spectroscopy (Hewlett Packard 4192-LF). Distinctly different impedance spectra were observed for nanocrystalline and coarsened samples (Fig. 2). Coarsened samples (Fig. 2a) exhibited two semicircular arcs characteristic of conductive grains and blocking grain boundaries, as previously seen in CeO_2 ⁶ and ZrO_2 ,⁷ while nanocrystalline samples (Fig. 2b) showed only a residual grain boundary arc. Taking bulk and boundary resistances from the intersections on the real axis of the corresponding arcs, and accounting for the factor of 500 difference in grain size, we find that the resistance per grain boundary is more than 10^3 lower in the nanocrystals. We

attribute this behavior to size-dependent grain boundary impurity segregation, wherein the boundary impurity concentration decreases with increasing interfacial area.^{8,9} In ZrO_2 , size-dependent segregation has been directly correlated with grain boundary impedance.⁸

Focusing on the bulk conductivity as the measure of volume defect behavior, we observe that the nanocrystal conductivity always increases with decreasing PO_2 , Fig. 3, as is characteristic of an n -type nonstoichiometric oxide. In contrast, the coarsened samples exhibit PO_2 -dependent nonstoichiometric behavior at very low PO_2 , but PO_2 -independent ionic conductivity at high PO_2 . This is characteristic of ceria (and zirconia) containing background acceptor impurities that pin the oxygen vacancy concentration at high PO_2 . Extrapolating the nonstoichiometric regime of the coarsened sample to high PO_2 , we find 10^4 greater electronic conductivity for the nanocrystal than expected for ideally pure coarse-grained ceria, indicating a proportionally greater nonstoichiometry.

The heat of reduction of each sample was determined from the temperature dependence of electronic conductivity within the PO_2 -dependent regime, Fig. 4. The nanocrystals show less than half the activation energy (0.99, 1.16 eV) of a coarse-grained sample (2.45 eV). The activation energy may be decomposed to obtain the heat reduction for the solid,

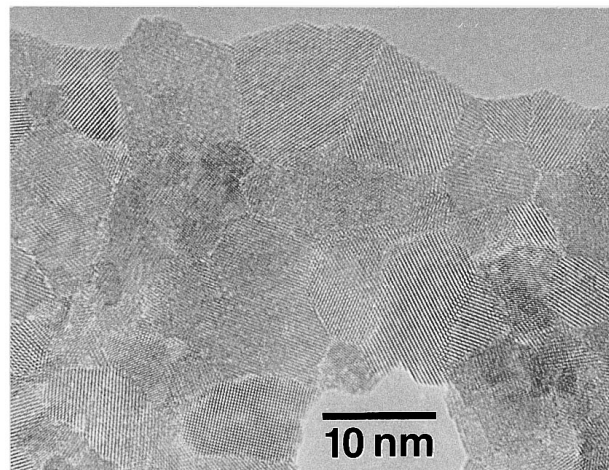


FIG. 1. HREM image (Topcon 002B instrument) of dense nanocrystalline CeO_{2-x} of 10 nm average grain diameter prepared from chemically processed (CP) powder.

^{a)}Department of Materials Science and Engineering.

^{b)}Author to whom correspondence should be addressed.

^{c)}Now at University of Missouri, Rolla, MO.

^{d)}Department of Chemical Engineering.

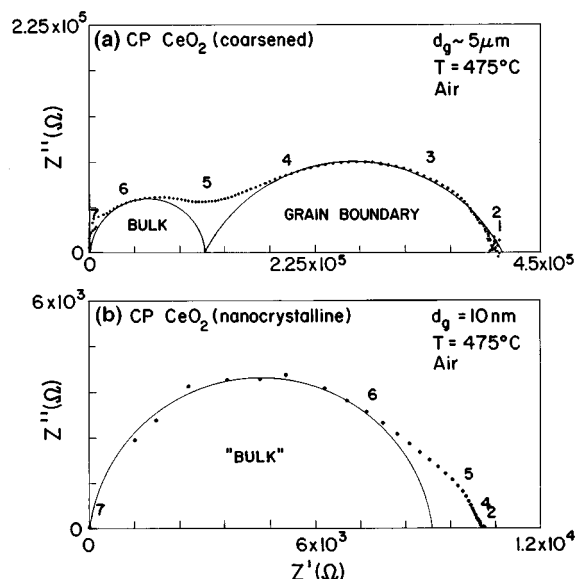


FIG. 2. Impedance spectra for (a) coarse-grained and (b) nanocrystalline CP ceria, showing a reduced low-frequency arc for blocking grain boundaries in the latter. Numerical labels give the logarithm of the measurement frequency (Hz).

using straightforward defect chemical analysis.^{4,10,11} Single crystal measurements¹² have shown that small deviations from stoichiometry in ceria are accommodated by doubly-ionized oxygen vacancies. For intrinsic materials, electroneutrality is given by $n=2[V_O]$, a $\log \sigma - \log PO_2$ plot is expected to show a slope of $-1/6$, and the $\ln \sigma T - T^{-1}$ plot (Fig. 4) yields an activation energy of $E_a = (\Delta H_1/3) + E_h$, where E_h is the electron-hopping energy (0.4 eV,⁴) and ΔH_1 is the heat reduction per oxygen vacancy. Under acceptor-doped extrinsic conditions, wherein electroneutrality is given by $[A'_{Ce}] = 2[V_O]$, the electronic component of conductivity should exhibit a PO_2 slope of $-1/4$, with an activation energy of $E_a = (\Delta H_1/2) + E_h$.

Comparing present results with literature data (Table I), the coarsened IGC material exhibits $\Delta H_1 = 4.10$ eV, in good agreement with the value for acceptor-doped ceria of 3.94 eV.¹¹ For the nanocrystals, the PO_2 slopes are between $-1/4$

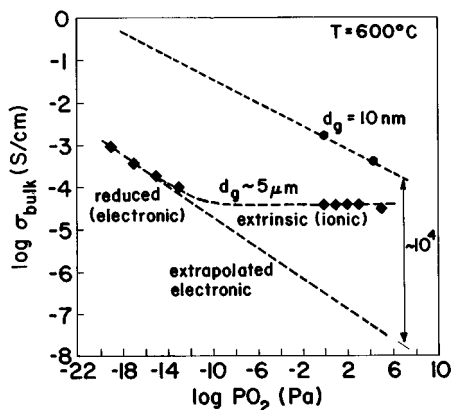


FIG. 3. The grain conductivity of a coarsened polycrystal exhibits electronic and ionic regimes as a function of PO_2 . In contrast, the nanocrystal conductivity follows electronic behavior characteristic of a reduced oxide even at high PO_2 , and is $\sim 10^4$ greater than the extrapolated electronic conductivity of the coarsened polycrystal at 600 °C.

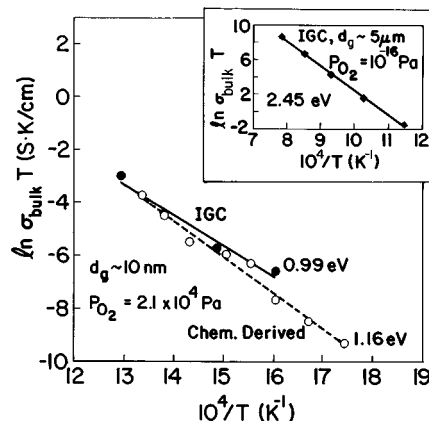


FIG. 4. The temperature dependence of conductivity, plotted for PO_2 ranges where samples exhibit reduced behavior, shows much lower activation energies for the nanocrystalline samples, corresponding to a heat of reduction that is over a factor of 2 lower.

and $-1/6$, indicating mixed defect control. We calculated ΔH_1 for both intrinsic and extrinsic defect compensation, and found that in either case, the heat of reduction is over a factor of 2 lower than the corresponding single crystal or polycrystal values, as shown in Table I. From the defect thermodynamics point of view, the nanocrystals can hardly be considered to be the same material as conventional ceria. We propose that grain boundary sites of lower vacancy formation enthalpy are the atomic-level origin of this behavior. Preferential reduction at interfacial sites results in charge-compensating electrons that then participate in the normal small-polaron conduction process.

In summary, we find that the defect and transport properties of nanocrystalline oxides are unique in two principal aspects. There is first a greatly reduced grain boundary impedance, which we attribute to size-dependent segregation. Since lattice concentrations of segregating species are also depleted when this occurs,⁹ the volume defect behavior of nanocrystalline oxides should be less impurity-sensitive. Second, the nonstoichiometry and transport properties of nanocrystalline ceria are clearly unique. In essence, defect thermodynamics dominated by interfaces are obtained in a bulk material. Similar behavior is expected in other materials of equivalently high specific surface area, including dispersed powders, whiskers, and very thin oxide films.

TABLE I. Defect thermodynamics for nanocrystalline and conventional ceria.

Sample	E_a (eV)	ΔH_1 (eV), per V_O	
		Intrinsic, $n=2[V_O]$	Extrinsic, $[A'_{Ce}]=2[V_O]$
Nanocrystalline, CP ^a	1.16	2.28	1.52
Nanocrystalline, IGC ^b	0.99	1.77	1.18
Coarsened, IGC ^b	2.45		4.10
Single crystal ^c	1.96	4.67	
Acceptor-doped polycrystal ^d	2.37		3.94

^aChemically-processed, from freeze-dried cerium acetate.

^bInert-gas-condensation processed.

^cFrom Ref. 10.

^dFrom Ref. 11.

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