

THE INFLUENCE OF GRAIN SIZE AND CHEMICAL COMPOSITION ON THE ELECTRONIC CONDUCTIVITY OF CERIA

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Undoped ceria (CeO_2) is a typical n-type conductor with a small polaron hopping conduction mechanism. From electrochemical point of view, the carriers of electrons were generated due to the redox reaction between Ce^{3+} and Ce^{4+} at elevated temperature or reducing conditions. However, very recently this reaction was reported in nanometer cerium dioxide (CeO_2), which resulted in some significant size-induced property changes, such as the Raman-allowed modes shifting and broadening; lattice expansion; the pressure-induced phase transformation; blue shift in ultraviolet absorption spectra etc. We have found that the interfacial resistance, electronic conductivity and lattice dynamics were all strongly related to grain size and the associated interfacial area. In this paper, an investigation of grain size (20nm – 5.0 μm) effects on those properties of the high purity CeO_2 and Gd doped CeO_2 . A series of impedance spectra and x-ray diffraction as a function of temperature and grain size were analyzed. Plots of $\log(\sigma)$ vs. $\log(p\text{O}_2)$ showed a slope $\sim 1/6$ for all grain size high purity undoped CeO_2 , which illustrated the intrinsic behavior due to $\text{Ce}^{3+}/\text{Ce}^{4+}$ reaction. An exponential increase of grain conductivity was observed in high purity undoped ceria when the grain size was decreased, which appears to result from two factors (1) an increase of carrier concentration (2) a decrease of the activation energy. Further studies showed an exponential decrease in the enthalpy of oxygen vacancy formation. For Gd doped CeO_2 , no significant change in the enthalpy was observed when the grain size was larger than 80nm.

Reference:

1. X. D Zhou and W. Huebner, Appl. Phys. Lett. 79, 3521 (2001).
2. X. D. Zhou, W. Huebner, I. Kosacki, and H. U. Anderson, Submitted to J. Am. Ceram. Soc.

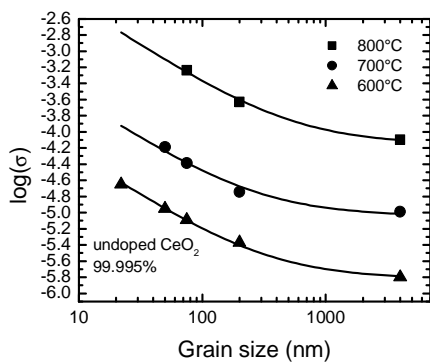


Fig. 1 Plots of $\log(\sigma)$ vs. grain size for high purity undoped CeO_2

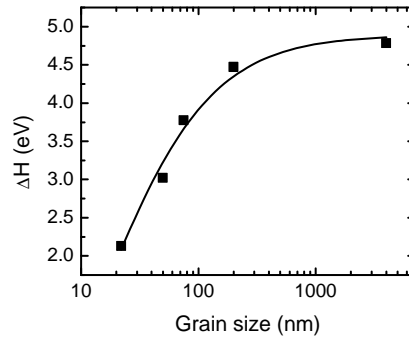


Fig. 2 The enthalpy of oxygen vacancy formation vs. grain size for undoped high purity CeO_2

