

Review

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: www.elsevier.com/locate/jalcom

Structure and properties of cerium oxides in bulk and nanoparticulate forms



CrossMark

ALLOYS AND COMPOUNDS

癯

Shruba Gangopadhyay^{a,b}, Dmitry D. Frolov^{a,c}, Artëm E. Masunov^{a,b,d,*}, Sudipta Seal^{e,f,g,a}

^a NanoScience Technology Center, University of Central Florida, 12424 Research Parkway, Suite 400, Orlando, FL 32826, USA

^b Department of Chemistry, University of Central Florida, 4111 Libra Drive, PS 255, Orlando, FL 32826, USA

^c Department of Chemistry, Moscow M.V. Lomonosov State University, Leninskiye Gory, Moscow 119991, Russia

^d Department of Physics, University of Central Florida, 4111 Libra Drive, PS 430, Orlando, FL 32826, USA

e Advanced Materials Processing and Analysis Center, University of Central Florida, 12760 Pegasus Drive, ENG1 381, Orlando, FL 32816, USA

^f Department of Materials Science and Engineering, University of Central Florida, 12760 Pegasus Drive, ENG1 207, FL 32816, USA

^g College of Medicine, University of Central Florida, 6850 Lake Nona Blvd, Orlando, FL 32827, USA

ARTICLE INFO

Article history: Received 28 April 2013 Received in revised form 5 August 2013 Accepted 3 September 2013 Available online 12 September 2013

Keywords: DFT Nanoceria Core-shell structure Cerium dioxide Oxygen vacancy

ABSTRACT

The experimental and computational studies on the cerium oxide nanoparticles, as well as stoichiometric phases of bulk ceria are reviewed. Based on structural similarities of these phases in hexagonal aspect, electroneutral and non-polar pentalayers are identified as building blocks of type A sesquioxide structure. The idealized core/shell structure of the ceria nanoparticles is described as dioxide core covered by a single pentalayer of sesquioxide, which explains the exceptional stability of subsurface vacancies in nanoceria. The density functional theory (DFT) predictions of the lattice parameters and elastic moduli for the Ce(IV) and Ce(III) oxides at the hybrid DFT level are also presented. The calculated values for both compounds agree with available experimental data and allow predicting changes in the lattice parameter with decreasing size of the nanoparticles. The lattice parameter is calculated as equilibrium between contraction of sesquioxide structure in the core, and expansion of dioxide structure in the shell of the nanoparticle. This is consistent with available XRD data on ceria NPs obtained in mild aqueous conditions. The core/shell model, however, breaks down when applied to the size dependence of lattice parameter in NPs obtained by the laser ablation techniques.

© 2013 Elsevier B.V. All rights reserved.

Contents

1.	Introduction	199
2.	Properties and structural relationships of cerium oxides	200
3.	Structure and properties of ceria nanoparticles and surfaces	203
4.	Interatomic potentials and first principles studies of bulk and nanoparticulate ceria.	203
5.	Hybrid density functional theory study of the bulk dioxide and sesquioxide	205
6.	Multiscale estimate of nanoparticle lattice parameters	206
7.	Conclusions	206
	Acknowledgments	207
	References	207

1. Introduction

* Corresponding author at: NanoScience Technology Center and Department of Chemistry, University of Central Florida, 12424 Research Parkway, Suite 400, Orlando, FL 32826, USA. Tel.: +1 407 374 3783.

E-mail address: amasunov@ucf.edu (A.E. Masunov).

Cerium oxide of variable composition is generally known as ceria. Its unique chemical and electronic properties make it an important material for number of applications. Easy shifting the Red/Ox equilibrium in ceria makes it an excellent catalyst for various chemical processes, including production and purification of

^{0925-8388/\$ -} see front matter @ 2013 Elsevier B.V. All rights reserved. http://dx.doi.org/10.1016/j.jallcom.2013.09.013

hydrogen [1], and carbon monoxide removal from the automobile exhaust [2]. Mobility of oxygen vacancies and consequently high ionic conductivity makes ceria a promising electrolyte for solid oxide fuel cells [3]. Electronic structure of ceria leads to its use as UV absorber in cosmetic industry and manufacturing of glass windows [4]. It is also used in light harvesting devices and optical displays [4]. In most of these processes the non-stoichiometry (the presence of oxygen vacancies) plays an essential role, especially when the properties are determined by the surface. In the latter case, films and nanoparticles (NP) make the most efficient use of this material. Resulting surface structure depends both on NP size, and on fabrication method. Films can be produced by several growth techniques, including electron beam evaporation [5-7], pulsed laser deposition [8–10], metaloorganic chemical vapor deposition [11], ion beam assisted deposition [12], and reactive magnetic sputtering [13]. Ceria thin films are used to fabricate. anode material for intermediate temperature solid oxide fuel cell. which allows to lower their operating temperature 500 °C [14]. Thin film of CeO₂ exhibits a high refractive index, and high dielectric constant, so it is a very promising material to use for optoelectrical, microelectronic, electro-optical devices [5]. The thin films of lanthanide doped ceria which are fabricated by using sol-gel technique are used for the electro-optical purposes [5,7]. The doped ceria films are transparent for the wave lengths of or above 500 nm and show no optical loss around 600 °C. Ceria thin films with a thickness about 100 nm are made by pulse laser ablation and used in optoelectronic devices.

In order to understand the structure and chemical properties of the oxygen vacancies, and subsequently the NP surface, we will review the properties of the bulk cerium oxides in Section 2. The surface effects and NP properties are considered in Section 3, with the emphases on lattice parameter increase for smaller ceria NPs. The relationship between bulk structures of cerium and its oxides are considered in Section 4, which serves as a foundation for the core/shell model for NP structure. In Section 5 we review different ab initio methods used in literature to simulate ceria in bulk and NP form. The Section 6 describes our hybrid Density Functional Theory approach, which we use to predict the lattice parameters and elastic moduli of the cerium dioxide and A type sesquioxide. Then in Section 7 we use the predicted values in conjunction with core/ shell NP model to estimate the trends in the lattice parameter as a function of NP size. These trends are compared to the experimental observations, and conclusions are made regarding the effect of the preparation conditions on nanoceria structure.

2. Properties and structural relationships of cerium oxides

Bulk cerium oxide has at least two stable stoichiometries, the dioxide (CeO₂) and dicerium trioxide (Ce₂O₃) which is commonly referred as sesquioxide. At ambient conditions dioxide crystallizes as CaF₂ (fluorite) type structure in face centered cubic space group *Fm*3*m* with the lattice parameter of 5.411 Å [15]. In that structure cerium ions occupy the vertices and faces of cubic unit cell. Each Ce(IV) is coordinated with eight oxygen ions arranged in a perfect cube, while each oxygen ion is surrounded by four cerium ions in tetrahedral arrangement. This structure is often described as cubic closed packing (ccp) of Cerium ions with oxygen ions occupying all tetrahedral holes. At the elevated pressure (31 GPa and room temperature) cerium dioxide undergoes phase transition from fluorite to cotunnite $(\alpha$ -PbCl₂) structure type with orthorhombic space group *Pnam* [16]. Another structural type $(\delta - Ni_2Si)$ had also been suggested [17]. Both α -PbCl₂ and δ -Ni₂Si types have similar positions of Ce ions and only differ in the position of oxygen ions. Unambiguous choice between these structural types is complicated by the fact that neither Raman spectroscopy, nor X-ray dif-



Fig. 1. Sandwich trilayer CeO₂: (a) top view; (b) side view. Ce atoms are in gold, O atoms are in blue, O atoms of the next trilayer are in light blue. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)



Fig. 2. Formation of the fluorite type structure as ABC stacking of CeO_2 sandwich trilayers. Ce atoms are in gold, O atoms are in blue, O atoms of the next trilayer are in light blue, triangular holes on the surface of the hexagonal layer are marked by pink triangles. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

fraction are sensitive enough to the position of light oxygen atoms in the presence of the heavy atoms. Based on the axial ratios, high pressure polymorph of cerium dioxide is more likely to belong to α -PbCl₂ structural type [17]. In α -PbCl₂ type structure the cation is surrounded by seven anions at roughly the same separation and two at a slightly larger separation (denoted as [7 + 2] coordination), while the anions coexist in two coordinations: one is four coordinate and the other is five coordinate [17].

In order to describe the relationship between fluorite and other structural types of ceria it is advantageous to consider a hexagonal aspect [18]. One can start with a hexagonal close-packed layer of cerium ions, then sandwich them between two hexagonal layers of O ions in ABC motif (here Ce layers are marked in bold). In this

Download English Version:

https://daneshyari.com/en/article/1612405

Download Persian Version:

https://daneshyari.com/article/1612405

Daneshyari.com