



Thermo-mechanical properties of cubic lanthanide oxides

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ABSTRACT

This contribution investigates the effect of the addition of the Hubbard U parameter on the electronic structural and mechanical properties of cubic (C-type) lanthanide sesquioxides (Ln_2O_3). Calculated Bader's charges confirm the ionic character of Ln–O bonds in the C-type Ln_2O_3 . Estimated structural parameters (i.e., lattice constants) coincide with analogous experimental values. The calculated band gaps energies at the U_{eff} of 5 eV for these compounds exhibit a non-metallic character and U_{eff} of 6.5 eV reproduces the analogous experimental band gap of cerium sesquioxide Ce_2O_3 . We have thoroughly investigated the effect of the O/Ce ratios and the effect of hafnium (Hf) and zirconium (Zr) dopants on the reduction energies of CeO_x configurations. Our analysis for the reduction energy of CeO_2 , over a wide range of temperatures displays that, shuffling between the two +4 and +3 oxidation states of Ce exhibit a temperature-independent behaviour. Higher O/Ce ratios necessitate lower reduction energies. Our results on Ce–Hf–Zr–O alloys are in reasonable agreements with analogous fitted values pertinent to lowering reduction energies and shrinkage in lattice parameters when contrasted with pure CeO_2 . Structural analysis reveals that Hf and Zr atoms in the solid solution are shifted towards the nearest vacancies upon reduction. It is hoped that values provided herein to shed an atomic-base insight into the reduction/oxidation thermodynamics of increasingly deployed catalysts for environmental applications.

1. Introduction

Over the last two decades, considerable attention has been devoted towards better understanding of properties that drive the unique applications of rare earth metals and their oxides. Lanthanide (Ln) oxides represent an array of materials that enjoy remarkable characteristics, such as high melting points of over 2000 °C, superior mechanical, thermal, optical and magnetic properties [1]. In earth elements, the unfilled 4f orbital is shielded from interactions with the adjacent atmosphere by the full octet of electrons in the $5s^2p^6$ outer shell [2]. The series of lanthanide oxides (Ln_2O_3) has emerged as promising materials in a wide range of applications, spanning in catalysis, antireflection coatings, ionic conductor industries [3–5], etc. Compounds of Ln_2O_3 have been in the centre of mounting interest as early as 1925 [6–11]. The two forms of cerium oxide (CeO_2 and Ce_2O_3) for instance have been the subject of numerous studies aiming to elucidate chemical and

physical characteristics of their bulk and thin films. Cerium oxides have been generally deployed as catalysts in the preparation of active metal nanoparticles [12,13], as electrolytes or as anode support materials [14]. Naturally, the lanthanide oxides occur in a sesquioxide form; however, in the case of Ce, Pr, and Tb oxides, they can also adapt other structural forms. Metallic Ce and Pr are readily oxidised into CeO_2 (ceria) and PrO_2 , respectively, in air, while under elevated oxygen pressures, Tb is found as Tb_4O_7 , and eventually transforms into TbO_2 [15].

Interestingly, it was revealed that, the Ln_2O_3 series exhibit a well-ordered periodicity in their physical attributes with the gradual filling of the 4f-electron shell, increasing from La to Lu. For example, a periodicity of band gap, E_g variation was found across this series [16]. The lattice structure of the sesquioxides at temperatures lower than 2000 °C falls into three distinct polymorphic forms: (a) A-type which assumes a hexagonal configuration with the $P-3m1$ space group symmetry, (b) B-

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type occurring in a monoclinic structure with the $C2/m$ space group symmetry, and (c) cubic C -type with the $Ia3$ space group symmetry [11,17].

An early experimental study by Templeton and Dauben [18] measured the lattice parameters of several lanthanide oxide samples with purity of > 99.9% (cubic: Mn_2O_3 type structure) from powder diffraction patterns with high accuracy. Recently, combinations of structural, mechanical, and optical properties, of rare earth oxides thin films produced by various synthesis techniques have been experimentally investigated. For instance, Dubau et al. [19], fabricated a large surface area cerium oxide films with thickness ≤ 30 nm using RF magnetron sputtering technique. They stated that, the structure and morphology of the deposited films was strongly affected by the oxygen concentration in the working gas utilized for the deposition process. Furthermore, optical and structural properties of Er_2O_3 films prepared by magnetron sputtering system have been studied by Miritello et al. [20]. Likewise, various characterization techniques have been utilized for the bulk and surface analysis of Ln_2O_3 . For instance, FTIR spectroscopy is a widely used characterization technique for the investigations of surface chemistry of lanthanide series using probe molecules such as H_2 and CO [21].

On the theoretical side, density functional theory (DFT) investigation [22] has elucidated an atomic-base insight into structures and electronic properties of Ln_2O_3 . Studied compounds include the A -type hexagonal structure and CeO_2 with the cubic fluorite structure (space group $Fm-3m$). Hirosaki et al. [5] attempted to screen the dependency of the volume per unit formula in A - and C -type structures on atomic numbers establishing an inverse relation. Nonetheless, recent theoretical advances have demonstrated that pure DFT methods utilized by Hirosaki et al. [5] are not capable of accurately describing the rather electronically highly correlated system of the Ln_2O_3 series. A very recent DFT investigation has been carried out by Richard et al. [17] with a focus on the pressure-induced C -type \rightarrow A -type phase transition. This study analyzed the crystalline structure, crystal equilibrium volumes, bulk modulus (B) and its first pressure derivative (B') as well as the electronic properties of these two phases. However, the study did not assess the mechanical stability of the Ln_2O_3 species nor utilized the obtained charge distribution to comment on the relative ionicity of the Ln -O bonds.

It has now become apparent that neat DFT methods [23,24], most notably the generalized gradient (GGA) and local density approximations (LDA), are unable to accurately describe the electronic structure in Ln_2O_3 . This is due to several deficiencies in standard DFT methods, for example, the lack of self-interaction cancellation, which results in reducing or even closing obtained band gaps. On this regard, GGA and LDA often underestimate corresponding experimental band gaps of Ln_2O_3 [15,25,26]. For example, Ce_2O_3 is incorrectly predicted by pure DFT methods as metallic (LDA) or a semiconductor with a small band gap (GGA) [22]. To overcome the severe delocalisations of $4f$ electrons in Ln_2O_3 systems by GGA and LDA functionals, an empirical (i.e., ad hoc) Hubbard U approach was developed; LDA + U /GGA + U [27,28]. Applying the self-interaction-corrected (SIC) or hybrid DFT approaches [29] provide accurate predictions for the electronic structures of d - and f -electronic systems as well. However, the DFT + U formalism proves to be a cost-effective approach choice that adequately overcomes the fundamental shortcoming of plain DFT. The empirical Hubbard U potential characterizing the strength of the on-site Coulomb interaction is not a universal value but rather an adjustable parameter, which is practically determined by fitting the calculated DFT + U values against analogous experimental data [30]. Examples of these fitted values include lattice constants [11], band gaps [15] and reaction energies [11].

Accruing various fundamental solid-state properties, such as

phonon spectra, specific heat, and thermo-elastic quantities is of fundamental importance when attempting to fine-tune characteristics of Ln_2O_3 towards real-life applications. From a chemical point of view, catalytic applications of lanthanide oxides rely on their remarkable capabilities to undergo a redox reaction in which the oxidation state switches from +4 to +3. In hydrogenation reactions of alkynes into olefins over CeO_2 , a crucial step is the stabilization of β - C_xH_y radicals caused by reduction of Ce surface atoms following adsorption of C_xH_y species [31]. The formation of partially reduced ceria surface was also a key mechanistic step in the reduction of SO_2 [32]. It follows that it is of a crucial importance to gain an insight into the thermodynamic feasibility pertinent to the redox cycle of the commonly deployed lanthanide oxides. A GGA + U study by Lutfalla et al. [33] has benchmarked the redox energy of CeO_2 against the corresponding experimental value for different U value, but only at 298.15 K. However, industrial applications of Ln_2O_3 -based catalysts typically occur at elevated temperatures.

It is well-known that cerium oxide CeO_2 plays a crucial role as an oxygen-storage component in many technologies, most notably in the three-way catalytic converters (TWCs) of automotive emissions [33]. The catalytic activity of the two stable states of ceria, namely Ce^{+4} and Ce^{+3} is linked with their ability to undergo a facile redox reaction. This in turn enables Ce-based catalysts to mimic analogous behaviour of noble metals [33]. In this regard, Ce-based materials serve as an oxygen buffer in prominent chemical reactions, most notably water-gas shift reactions, hydrocarbon oxidation and NO_x conversion into nitrogen [34,35]. The thermodynamic feasibility of the redox cycle – as will be demonstrated in Section 3.3 was shown to strongly depend on the O/Ce ratios as well as on the existence of doped Hf and Zr in the alloys of Ln_2O_3 .

The catalytic interaction of various chemical species with the reduced and stoichiometric low CeO_2 (111) surface has been the subject of many theoretical investigations. For instance, the DFT + U work by Fernández-Torre, J., et al. [36] addressed the dissociation of molecular hydrogen, atomic hydrogen diffusion and clustering on the CeO_2 (111) surface. They found that dissociation of H_2 occurs at reaction barrier of only 1.0 eV (i.e., 96 kJ/mol, kilojoule per mole O_2). Diffusion of an atomic hydrogen adsorbed on a surface oxygen atom to the third layer was found to be noticeably endothermic by ~ 1.8 eV. Chen et al. [37] plotted reaction profiles for the hydrogen cycle over the two stoichiometric and reduced CeO_2 (111) and CeO_2 (110) surfaces. In our very recent work, we establish thermo-kinetic parameters for the dissociative adsorption of three chlorinated volatile organic compounds (CVOCs), namely chloroethene (CE), chloroethane (CA) and chlorobenzene (CB) [38] over the CeO_2 (111) surface. Our findings indicate that direct fission of the Cl–C bonds prevails over surface-assisted elimination of HCl molecules. Likewise, chlorine transfer from the surface into the adsorbed cyclic moieties signifies a viable chlorination route. However, ceria may also play a dual role in the destruction/formation of aromatic pollutants as it strongly fixes phenyl radicals; a crucial step in the surface-mediate formation of dioxin-type compounds [39,40].

The unique contribution of this study is comprehensive DFT + U accounts into the electronic structures and mechanical properties of C -type lanthanide sesquioxides. The aim of this work is fourfold: (1) to evaluate the effects of the Hubbard U parameter on the electronic and structural properties of C -type lanthanide sesquioxides (Ln_2O_3), (2) to assess the mechanical stability of all C -type lanthanide sesquioxides, (3) to elucidate the thermodynamic feasibility of CeO_2 to undergo a redox reaction at temperatures relevant to catalytic applications, and (4) to underpin the effect of adding Hf and Zr impurities on the reduction energies of CeO_8 [$\delta = 2$ –1.5]. To the best of our knowledge, $\Delta G(T)$ values for reduction of any Ln_2O_3 have not been elucidated so far in the

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