J. At. Mol. Sci.
doi: 10.4208/jams.081109.091809a

Vol. **1**, No. 2, pp. 143-151
May 2010

Elastic and optical properties of CeO_2 via first-principles calculations

Li-Li Sun[a], Yan Cheng[a,*], and Guang-Fu Ji[b,*]

[a] *School of Physical Science and Technology, Sichuan University, Chengdu 610064, China*
[b] *Laboratory for Shock Wave and Detonation Physics Research, Institute of Fluid Physics, Chinese Academy of Engineering Physics, Mianyang 621900, China*

Received 11 August 2009; Accepted (in revised version) 18 September 2009;
Available online 19 April 2010

Abstract. The elastic and optical properties of the cubic CeO_2 and its behavior under pressure are investigated by using the local density approximation (LDA). The computational results are found in good agreement with the available experimental data and other theoretical results. The optical properties including dielectric function, absorption, reflectivity and refractive index are calculated and analyzed. It is found that CeO_2 is transparent from the partially ultra-violet to the visible light area and the transparence is hardly affected by the pressure. Furthermore, the curve of optical spectrum shifts to high energy area (blue shift) with increasing pressure.

PACS: 71.15.Mb, 62.20.dq, 78.20.Ci
Key words: density functional theory, elastic properties, optical properties, CeO_2

1 Introduction

As a rare-earth oxide, cerium oxide forms an interesting and extensively studied series, and has numerous applications in technology. For example, as one of the non-stoichiometric oxides [1], CeO_2 is extensively used in the modern catalytic industry due to its high oxygen storage capability [2–7]. It is the major component in catalytic converters to reduce harmful emissions from automobile exhausts [2], and has been often used as a promoter in an automotive exhaust catalyst for purifying carbon monoxide (CO), nitrogen oxides (NO_x) and hydrocarbon (HC) [4–9]. The automotive catalyst system has been operated under the conditions of a certain range of air/fuel (A/F) ratio . The CeO_2 can provide oxygen for oxidizing CO and HC under rich A/F conditions, and remove it

*Corresponding author. *Email address:* yan.cheng@126.com (Y. Cheng); cyfjkf@caep.ac.cn (G. F. Ji)

from the exhaust gas phase for reducing NO_x under lean A/F conditions [10]. It is also found that the CeO_2 is of the potential interest as optical component materials and laser hosts [11–14] and as prospective materials for future microelectronic applications [15].

Although CeO_2 has long been utilized as a material for oxygen storage [2–7], first-principles calculations on CeO_2 have hitherto been prohibitive, not least because of the difficulty in describing or converging the localized f valence electrons [16]. As fundamental issues and key features of cerium oxides CO_2, like the occupation of the $4f$ orbital and bonding, have been investigated by a number of experimental techniques [11,17]. In the early 1980s, Koelling *et al.* [18] calculated the electronic structure of CeO_2 by means of the linear augmented-plane wave (LAPW) method with Slater exchange and warped muffin-tin approximation for the crystal potential and charge density. They reported that the f and d states of Ce atom are hybridized with the oxygen $2p$ bands.

Hill and Catlow [19] investigated CeO_2 by the restricted Hartree-Fock method, which is well known for describing the exchange interaction correctly but entirely missing the correlation effects [20]. More recently, Skorodumova *et al.* [21] have calculated the electronic, structural, bonding, optical and magnetic properties of CeO_2 by means of the full-potential linear muffin-tin orbital (FP-LMTO) method in the framework of the density functional theory (DFT). They showed that in the case of CeO_2 their calculated density of states, optical transitions and electron localization function indicate that the unoccupied $4f$ states of Ce can be considered as essentially equivalent to an empty atomic like $4f$ level. Also, Fabris *et al.* [22] investigated on the defective CeO_2 by modeling multiple valence compounds using density-functional theory.

In this work, we give a detailed description for the elastic and the optical properties of CeO_2 through the Cambridge Serial Total Energy Package (CASTEP) program [23,24]. The structure and elastic constants obtained here are in agreement with the experimental data and other theoretical results. The elastic and optical properties of CeO_2 as well as their behavior under pressure have also studied.

2 Theoretical method

2.1 Total energy electronic structure calculations

In our electronic structure calculations, we adopt the non-local ultrasoft pseudopotential introduced by Vanderbilt [25] for the interactions of the electrons with the ion cores, together with the local density approximation (LDA) [26]. The electronic wave functions are expanded in a plane wave basis set with energy cut-off of 480 eV. For the Brillouin-zone k-point sampling, we use the Monkhorst-Pack mesh with $10\times10\times10$ k-points. It is found that these parameters are sufficient in leading to well converged total energy, geometrical configurations and elastic stiffness coefficients.