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Ab Initio Study of Three Phases of Zirconium Oxide ZrO_2 and Fuorite-Related Zirconium Oxynitride Zr_2ON_2 †

Mourad Azibi* and Nadia Saoula

CDTA, Cite 20 aout 1956 Baba Hassen, Algiers, Algeria;

* Correspondence: author: mazibi@cdta.dz

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In recent years, there has been a growing interest in replacing metallic parts in heat engines by structural ceramics such as zirconium dioxide (ZrO_2) [1]. However, the high-temperature form of ZrO_2 with the fluorite structure and high oxide ion mobility is unstable at room temperature. One approach to stabilise the fluorite structure of ZrO_2 is aliovalent substitution of Zr^{4+} by Y^{3+} or Ca^{2+} [2,3]. As well as stabilising the fluorite structure, this introduces anion vacancies enhancing the oxide ion conductivity. A second approach is to make an anion substitution of O^{2-} by N^{3-} to make a series of zirconium oxynitrides which will have anion vacancies [4].

The band structures, density of states and optical properties of zirconium dioxide (ZrO_2) in the monoclinic, tetragonal and the cubic phases and the fuorite-related zirconium oxynitride (Zr_2ON_2) have been calculated using the density functional theory with the generalized gradient approximation (GGA) parameterized with the revised Perdew-Burke-Ernzerh for solids (PBESOL) as an exchange correlation function [5]. Band gaps of 3.97, 4.01 and 1.55 eV are obtained respectively for these phases. The underestimation of band gaps by DFT is common, which exists due to the limitation of predicting conduction band properties. As a result, the conduction band minimum of Zr_2ON_2 is reduced compred to ZrO_2, which makes Zr_2ON_2 active under visible light irradiation.

For the ZrO_2 structures, the valence bands and the lower conduction bands are all quite similar but become more fiat in going from the cubic to the monoclinic phase. The valence bands are composed with an higher mixed O 2p, Zr 4d orbitals of about 4–6 eV width. The conduction band is mainly derived from the Zr 4d orbitals. For the Zr_2ON_2 fluorite structure, the valence band maximum mostly consists of O 2p and N 2p states which are strongly hybridized with Zr 4d orbitals, while the bottom of the conduction band is composed of a Zr 4d state overlap with O 2p and N 2p. Strong hybridization means potential covalent bonding and a less ionic character. A covalent bond between O or N and the Zr atom can be seen when the O 2p and N 2p states hybridized with Zr 4d between −5.5 eV and 0.0 eV.

The optical properties of ZrO_2 and Zr_2ON_2 are calculated by the dielectric function $\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega)$. The Kramer–Kronig relation is used to obtain the real parts of the dielectric function from imaginary ones. Optical properties such as refractive index n (ω), extinction coefficient k (ω), reflectivity R (ω) and absorption coefficient I (ω) are calculated from the dielectric constant.

The average value of the refractive index of Zr_2ON_2 is 1.7 at the static limit, $n^{average}$ (ω), and 2.0 at 650 nm. Our calculations show better agreement with the experimental value, 2.2 at 650 nm [6]. The refractive indices increased beyond the zero frequency limits

and reached their maximum values. Beyond the maximum value they start to decrease and with a few oscillations they go beyond unity. The absorption coefficient, I (ω), measures the penetration of light through materials before it gets absorbed. The I (ω) rapidly increases above 100 nm for ZrO_2 and 150 nm for Zr_2ON_2. Absorption also occurs in the visible region, which indicates that Zr_2ON_2 is an active photocatalyst under visible light irradiaton and the absorption band extends from 150 nm to 550 nm.

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