Doping effect of sulfur substituting on Zirconium dioxide ZrO2

Samira Idrissi[1], soumia ziti[2], labrim hicham[3], and Bahmad Lahoucine[4]

[1]Mohammed V University of Rabat
[2]Intelligence Artificial and Security of Systems, Mohammed V University of Rabat, Faculty of Sciences, B.P. 1014 Rabat, Morocco.
[3]USM/DERS/Centre National de l'Energie, des Sciences et des Techniques Nucléaires (CNESTEN), Rabat, Morocco.
[4]Laboratoire de la Matière Condensée et des Sciences Interdisciplinaires (LaMCScI), Mohammed V University of Rabat, Faculty of Sciences, B.P. 1014 Rabat, Morocco.

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Abstract

In this paper, we use the density functional theory (DFT) calculations under Quantum Espresso package to characterize the doping effect of sulfur substituting on the Zirconium dioxide ZrO2. Through the density of states and the band structure calculations, a direct band gap is appearing for the pure and doped studied system. The electronic properties analysis shows that the doping with sulfur could considerably decrease the band gap of doped ZrO2 by the presence of an impurity state of sulfur 3 p on the up spin of the valence band. The results of the ab-initio density functional theory investigations show that the substitutional sulfur dopants incorporated into the Zirconium dioxide ZrO2 drastically and affect the electronic structure of the studied material. In fact, the doping of Zirconium dioxide ZrO2 with appropriate concentration values of sulfur leads to band gap values in the interval (1-2) eV. We recall that the band structure and density of states can improve among others: the energy gap of this doped ZrO2 material. In fact, we have started from 1.3 eV for the pure ZrO2 to reach 1.2 eV for 9% of sulfur doping. This last energy gap value is suitable for photovoltaic application.

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S. IDRISSI[1,*], S. ZITI[3], H. LABRIM[2] and L. BAHMAD[1,*]

[1] Laboratoire de la Matière Condensée et des Sciences Interdisciplinaires (LaMCScI), Mohammed V University of Rabat, Faculty of Sciences, B.P. 1014 Rabat, Morocco.

[2] USM/DERS/Centre National de l'Energie, des Sciences et des Techniques Nucléaires (CNESTEN), Rabat, Morocco.

[3] Intelligence Artificial and Security of Systems, Mohammed V University of Rabat, Faculty of Sciences, B.P. 1014 Rabat, Morocco.

Abstract: 11[*]) Corresponding authors:*samiraidrissi2013@gmail.com (S. I)* ;*lahou2002@gmail.com (L.B)*;

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We recall that the band structure and density of states can improve among others: the energy gap of this doped ZrO2 material. In fact, we have started from 1.3 eV for the pure ZrO2 to reach 1.2 eV for 9% of sulfur doping. This last energy gap value is suitable for photovoltaic application.

Keywords: Zirconia ZrO2; Doping; Band gap; gradient generalized approximation (GGA); DFT method.

Introduction

As an essential ceramic compound, zirconium dioxide (ZrO2) has attracted immense attention, because of its higher refractory, thermal and mechanical properties [1- 7]. For the applications of light solar cells, the nanotechnology has focused on enormous improvement in the procedure of semiconductor nano-materials [8-12]. Because of the low production cost [13, 14], the development of renewable energy resources have a large interest in prepared solar cell technology owing to high power conversion efficiency.

On the other hand, the metal oxide layers such as Al2O3, TiO2, SiO2, MgO2, and ZrO2 have been used to act as an energy barriers forrestraining charge recombination [15-20]. In visible and near infrared region (NIR), the Zirconia dioxide material ZrO2 host possesses a high physical, chemical stability and optical transparency. The energy transfer from ZrO2 to rare earth ions has been proved by different doping ions such as Yb 3p, Er 3p,Tm 3p, Tb 3p, Eu 3p and Ho 3p [21-24]. In addition, the ZrO2 might be a good spectrum modifying matrix serving as a photon-conversion and an electron transporting layer. Therefore, the over coating of co-doped Yb-3p and Er-3p have the wide band gap value (4-6 eV) of the material ZrO2 [26-27]. The charge recombination participates to the loss of charge carriers and therefore decreases the photovoltaic performance of the cell [28-35].

Moreover, the several efforts on studying [36-38] have been devoted to the study of ferromagnetism tempted by the transition metal doping of semiconductor oxides ZrO2, called diluted magnetic semiconductors (DMSs) [39-40]. Because of the ferromagnetism in semiconductor metal oxides discovers, main applications in spintronics and optoelectronics are achieved. However, it remains unclear whether ferromagnetism is an intrinsic property of the system or it is due to the combination of magnetic impurities [41, 42]. Also, the Oxides ZrO2 have been also predicted as ferromagnets at room temperature when doped by the light 2p elements (N) [43].

The aim of this work is to analyze and discuss the band gap values of the zirconium dioxide ZrO2 by doping this material with different concentrations of the sulfur element (S). In fact, the doping sulfur is an efficient method for narrowing the band gap energy of semiconductor oxide and shifts the threshold wavelength to the visible light region, see Refs. [44-45]. This could be helpful to use solar energy for the elimination of organic hazards by photocatalysis.

In the present study, the effect of doping this material has been discussed, as function of the different concentrations: doped ZrO2 with 5 %, 9 %, 14 % and 18% of sulfur. These concentrations are below the percolation threshold of the pure dioxide ZrO2 compound. For this purpose, we study such properties by using the DFT method under the Quantum Espresso package.

Crystal structure and calculation method

In this paper, we are discussing the results of doping effect of Sulfur on Zirconium dioxide ZrO2. The structure of the pure Zirconium dioxide ZrO2 as demonstrated in Fig. 1, by the Xcrysden package [46]. The ZrO2 has the cubic structure with the space group "Fm3m" (N° 225). The lattice constant is chosen to take the value 5.149 Å [47] and very near to the other theoretical studies 5.139 and 5.154 Å [48, 49]. The zirconium atoms are occupying (0, 0, 0) while the oxygen atoms reside in positions: (1/4, 1/4, 1/4) and (3/4, 3/4, 3/4).

To study the doping effect of sulfur substituting on the Zirconium dioxide ZrO2. Through the density of states and the band structure calculations of the pure and doped zirconium dioxide ZrO2 with sulfur. We apply the Abinitio method using the Quantum Espresso code [50]. In fact, the obtained calculations are established based on the Density Functional Theory (DFT).

Indeed, we executed our simulations under the ultra-soft pseudo-potential method [51]. In these numerical calculations, we have used the gradient generalized approximation GGA founded on the parametrization given by Perdew et al. [52]. We use this approximation to treat the exchange correlation functional.

The valence electron configuration for Zirconium (Zr), oxygen (O) and sulfur (S) are: Zr (4d 5s), (2s 2p) and (3s 3p), respectively. The electrons were treated explicitly as valence states and expanded in plane-waves. In this work, the cutoff energy is equivalent to the separation of valence and core configurations, this value is found to be about 340 eV. The special points sampling integration, in the Brillouin zone, were employed using the Monkhorst–Pack method [53]. The convergence tolerance, in our simulations are fixed to 10^{-6} eV/atom. Some of our recent works have been based on the DFT study and other methods of numerical simulations [54-57].

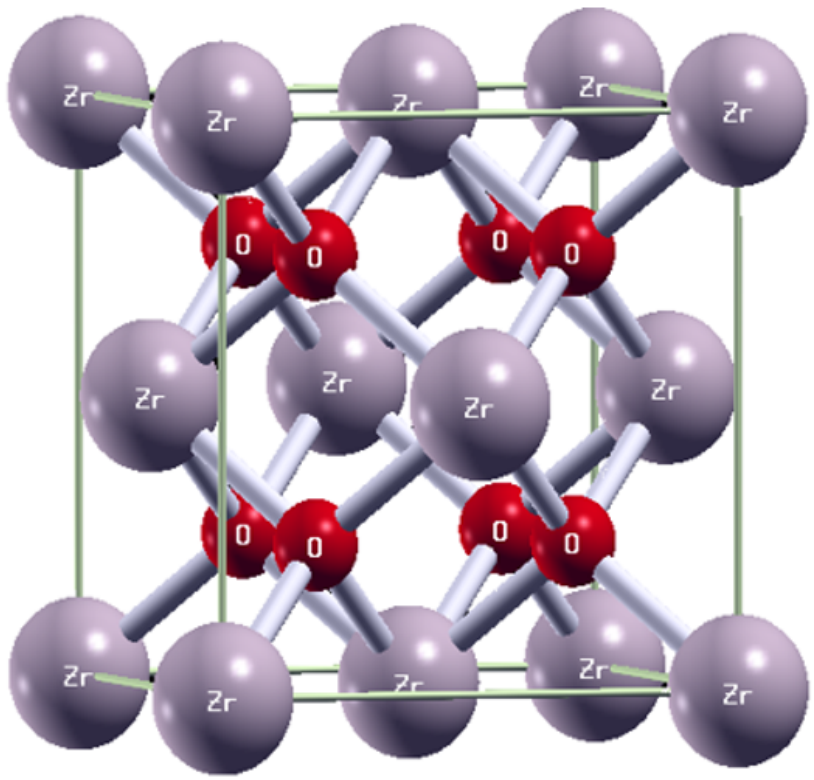

Fig.1: Schematic representation of the pure Zirconium dioxide ZrO2 using the Xcrysden package [46].

Results and discussions

The total and partial density of states (DOS) of the pure zirconium dioxide ZrO2 have been plotted in order to explore the electronic behavior of the studied system.

The values of the electronegativity between the Zr and O elements are very different, while such values are: 1.33 for Zr atoms and 3.44 for O atoms. The difference between such values is equal to 2.11 which is larger than 1.7 on the Pauling scale. Additionally, the studied material is characterized by the ionic bonding. This ionic chemical bonding behavior can be explained by using the partial DOS from shown in Fig. 2 (a). From

this figure, the 2p orbitals of O and 4d of Zr are different below and above Fermi level. In fact, the 2p states of O dominate below the Fermi level, while in the above Fermi level, the 4 d states of Zr are dominating.

Moreover, Fig.2 (b) shows that this material does not present any magnetic behavior, since a perfect symmetry is present between up and down density of states. Also, this compound is a semiconductor with a direct band gap value [?] 3.1 eV. On the other hand, Fig.2 (c) presents the band structure of the pure ZrO2. This figure presents a direct band gap at the G point and confirms the value of the band gap of the pure ZrO2 found in Figs.2 (a) and 2 (b).

Such results are in good agreement with other theoretical calculations such as the value 3.09 eV using VASP program [58] while for the monoclinic phase the obtained value is located between 3.4 and 5.4 eV using (SIESTA) package [59].

On the other hand, Figs. 3 (a), 3 (b) and 3 (c) provide the obtained results of doping the dioxide ZrO2 with 5% of sulfur. In fact, Fig.3 (a) illustrates partial density of states showing the orbitals

Zr-(4d), O-(2p) and S-(3p). This figure shows also that the contribution of the partial density of states orbital O-(2p) is dominating in the valence band, while the contribution of the partial of density of states of Zr-(4d) is important in the conduction band region.

Moreover, Fig.3 (b) shows that the doping with 5% of sulfur make appearing a band gap value of 2.3 eV. Also, a perfect symmetry between spin-up and spin-down confirms the non-magnetic character of the doped zirconium dioxide ZrO2.

In addition, the band structure shown in Fig.3 (c) confirms the band gap value (2.3 eV) predicted in Figs.3 (a) and 3 (b). Similarly, to the Fig.2 (c), a direct band is found at the G point in Fig.3 (c).

Moreover, the existing experimental works showed that the formation of Zr–S bonds causes a decrease of the band gap from 3.38 eV to 2.46 eV [60]. When increasing the doping concentration values of sulfur atoms, the band gap decreases as it is shown Figs. 4 (a), 4 (b) and 4 (c). Such figures are plotted for 9% of sulfur concentration and predict a band gap value: 1.2 eV. This band gap decreases to achieve the value 0.6 eV as it is illustrated in Figs. 5 (a), 5 (b) and 5 (c) when doping with for 14% of sulfur. This band gap disappears when the doping concentration reaches value 18 % of the doping with sulfur as it is presented in Figs. 6 (a), 6 (b) and 6 (c).

Our results of band gap values of pure and doped zirconium dioxide ZrO2 are summarized in table 1 for the concentration values: 5%, 9%, 14% and 18%. This table reproduces the already mentioned results from different figures.

To complete this study, we present in Fig.7 the energy and band gap of the doped ZrO2 as a function of different concentrations (%) of sulfur atoms. From this figure, it is clear that when increasing the doping concentration of sulfur the band gap energy decreases. While the total energy of the studied system increases when increasing the sulfur concentration.

It is worth to note that the band gap value 1.2 eV, which useful for photovoltaic applications, which is reached for 9% of sulfur concentration.

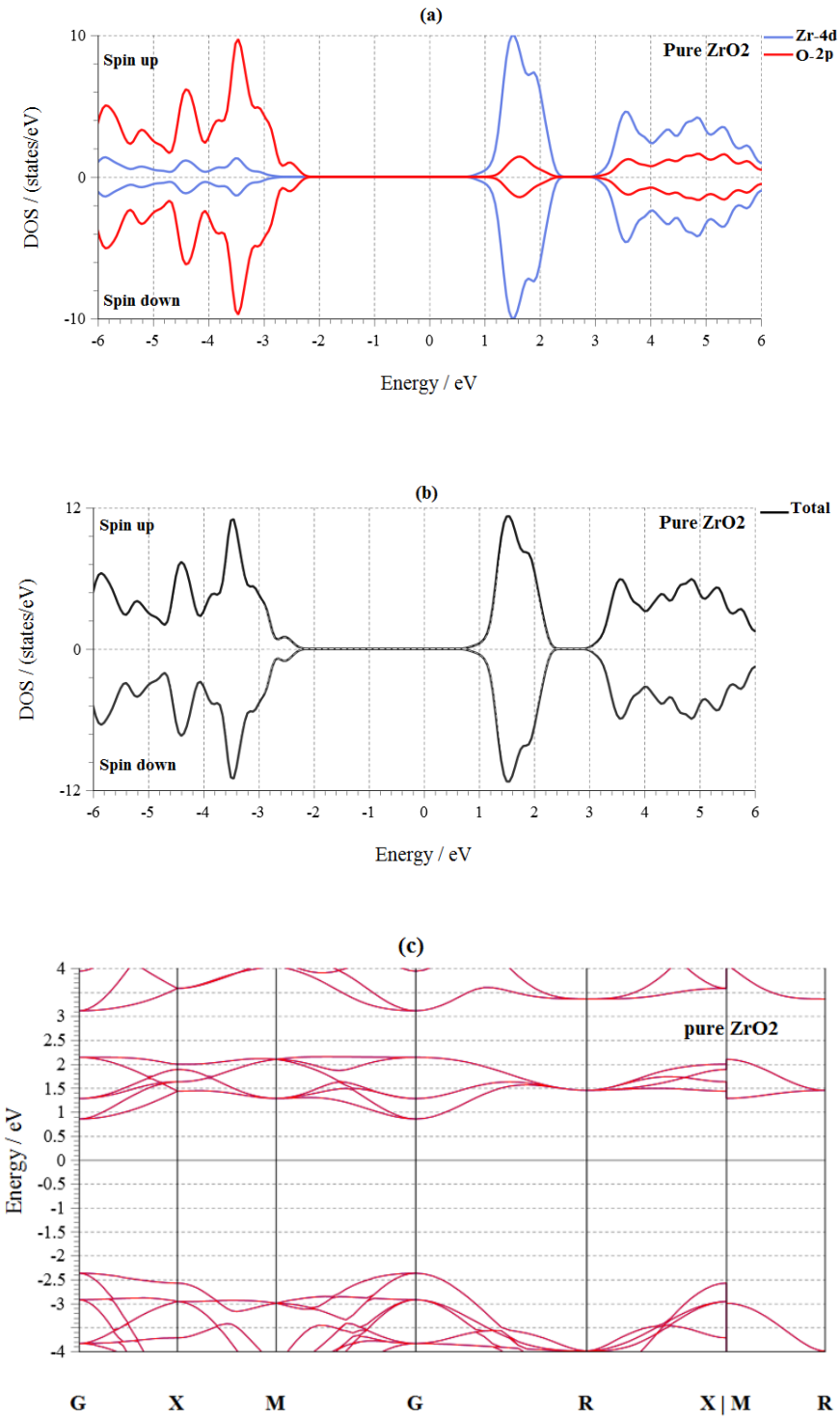

Fig.2: the pure ZrO2, partial density of states (DOS) in (a), Total DOS in (b) and Band structure in (c).

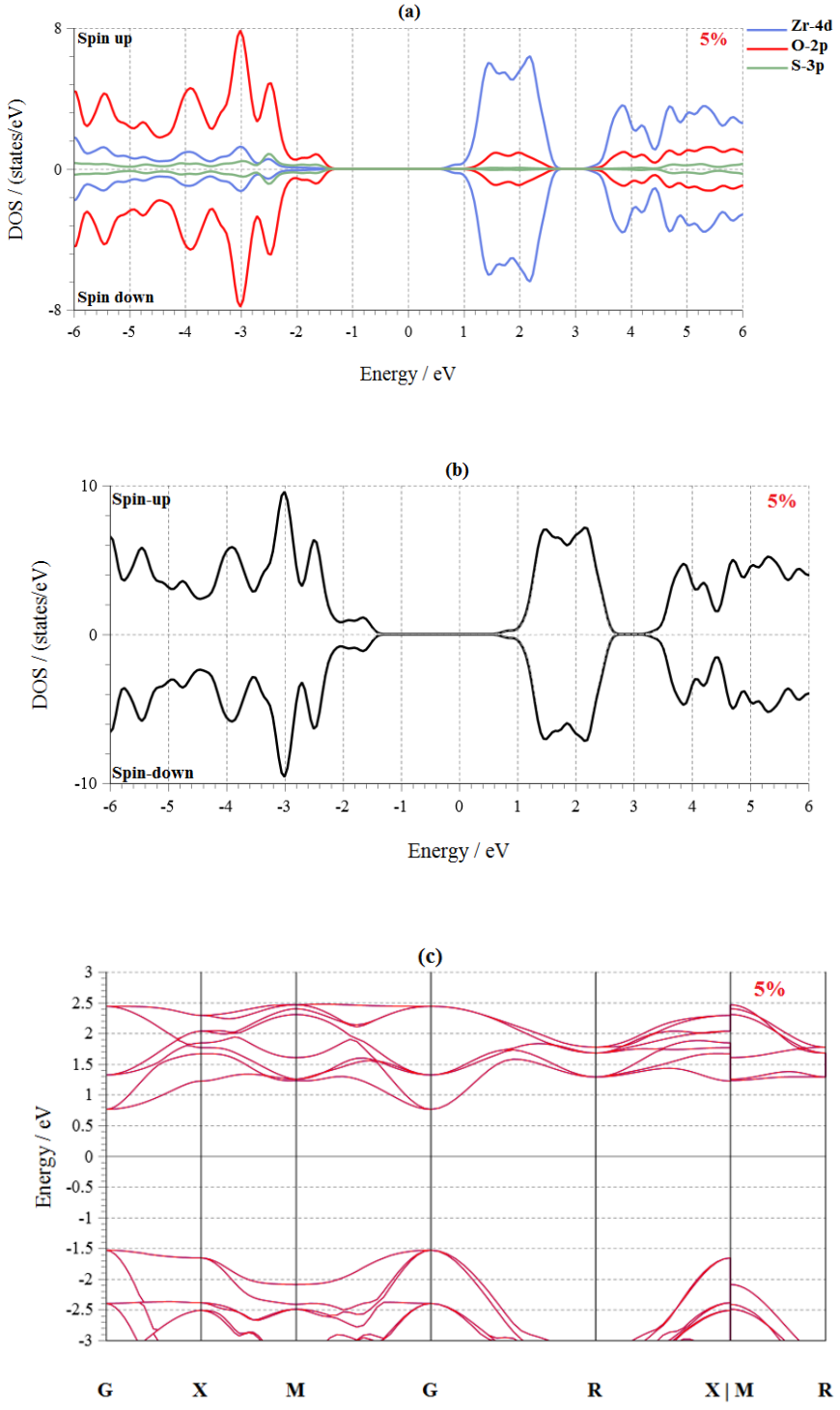

Fig.3: Doped ZrO2 with 5% of Sulfur, partial density of states (DOS) in (a), Total DOS in (b) and Band structure in (c).

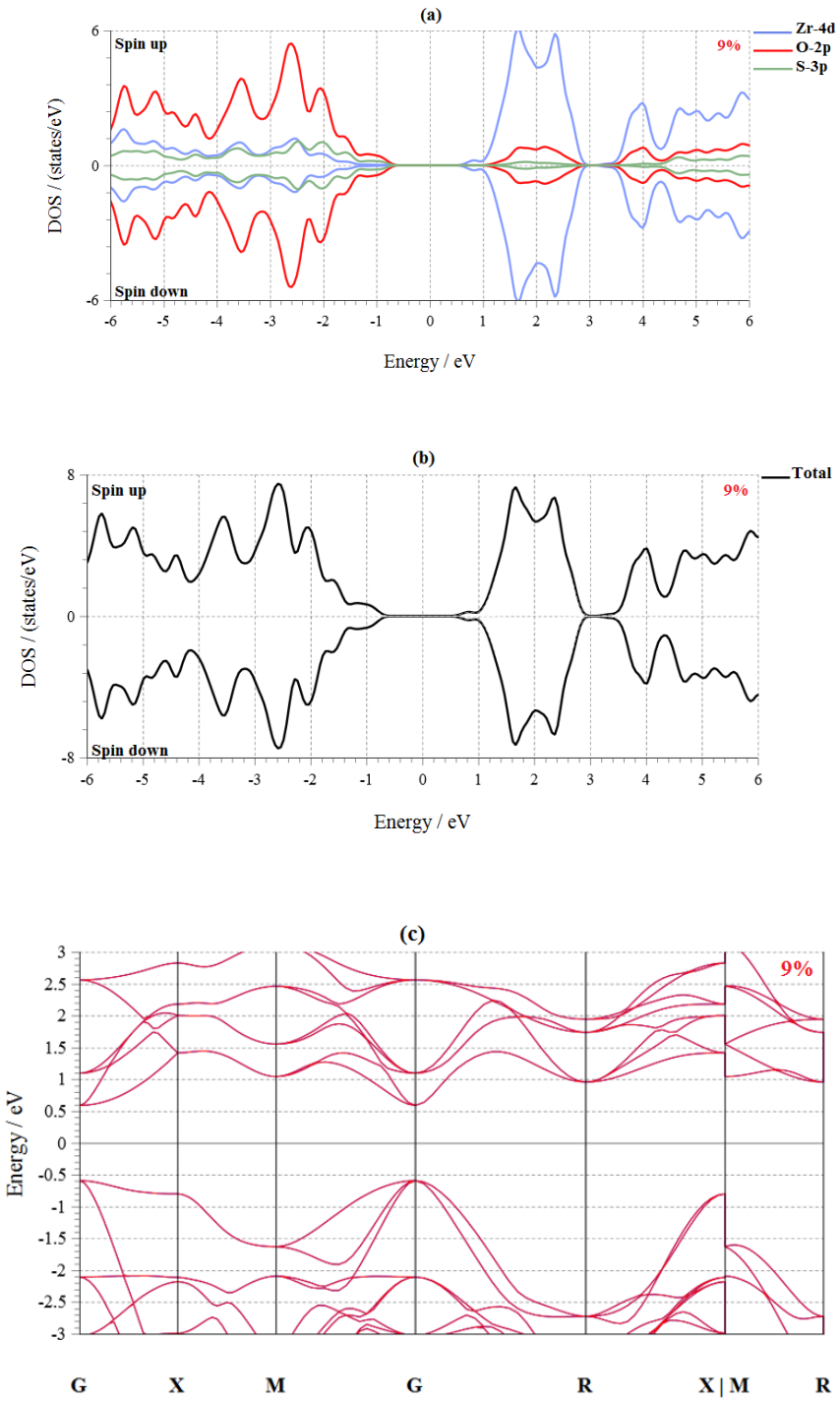

Fig.4: Doped ZrO2 with 9% of Sulfur, partial density of states (DOS) in (a), Total DOS in (b) and Band structure in (c).

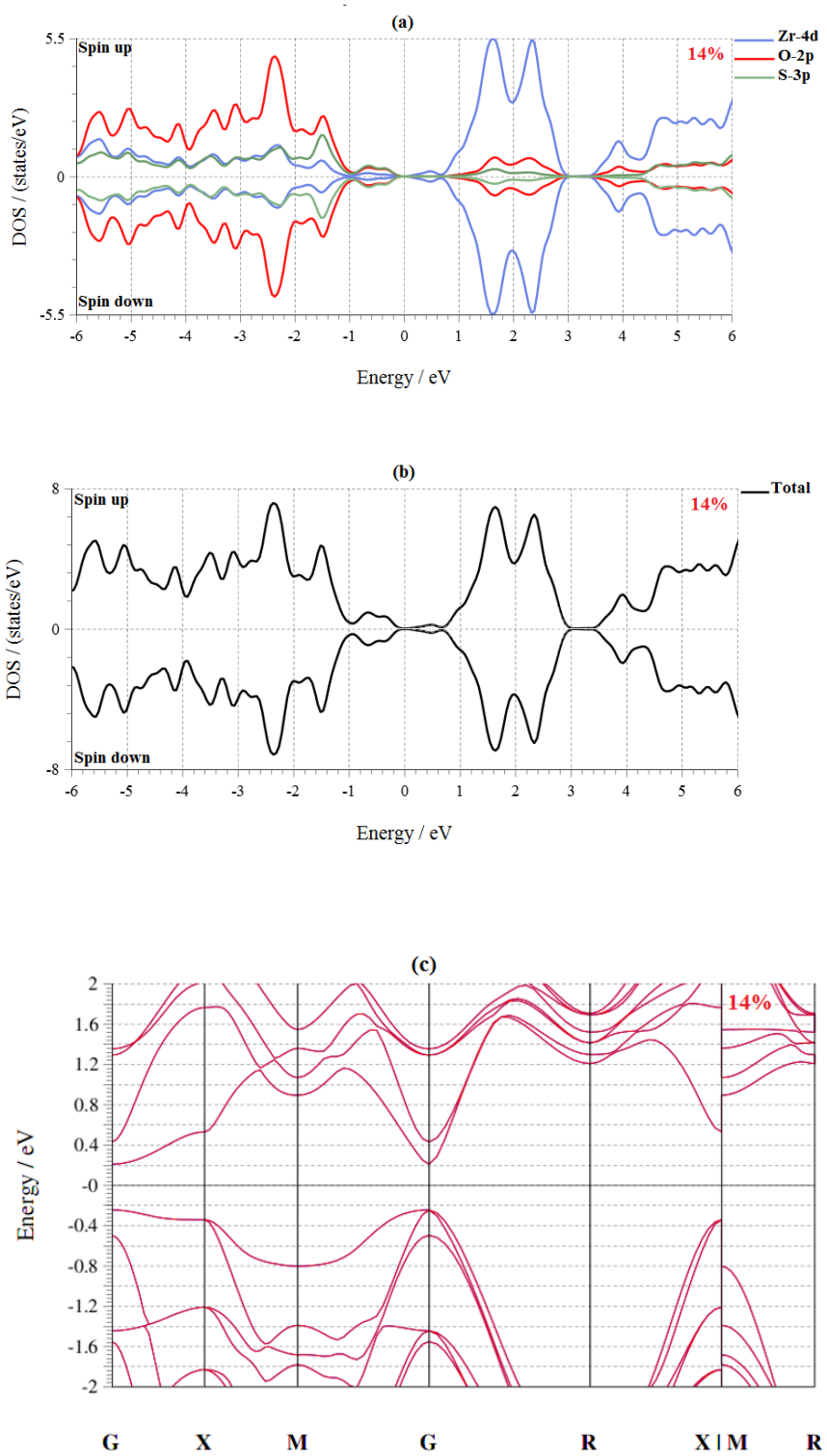

Fig.5: Doped ZrO2 with 14% of Sulfur, partial density of states (DOS) in (a), Total DOS in (b) and Band structure in (c).

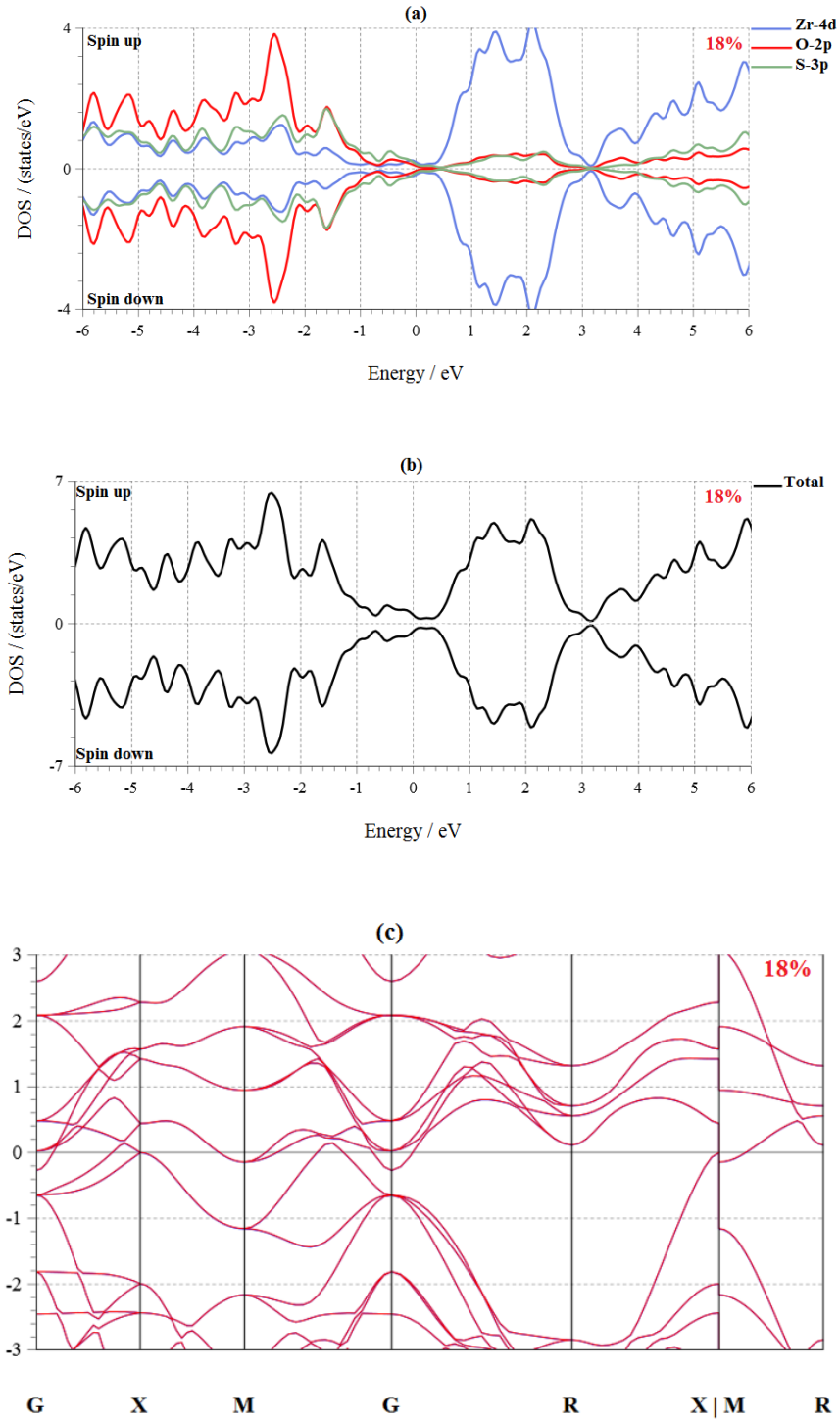

Fig.6: Doped ZrO2 with 18% of Sulfur, partial density of states (DOS) in (a), Total DOS in (b) and Band structure in (c).

Fig.7: Energy and band gap of the doped ZrO2 as a function of concentration (%) of impurities of sulfur.

Sulfur doped ZrO2	Eg (eV)
Pure case	3.1 present work 3.09 [58] 3.4 [59] 3.38 [60]
5 %	2.3
9 %	1.2
14 %	0.6
18 %	–

Table 1: Band gap values of the pure and doped zirconium dioxide ZrO2.

IV. Conclusion

In this paper, we have illustrated and discussed the effect of sulfur doping of the zirconium dioxide ZrO2. In fact, we have applied the gradient generalized approximation GGA. This material dos not present any magnetic behavior, since a perfect symmetry is present between up and down density of states. Also, this pure material is a semiconductor with a direct band gap value 3.1 eV. The used concentrations of sulfur doping are: 5%, 9%, 14% and 18%. Such concentration values are below the percolation threshold. Moreover, the doping with 5% of sulfur make appear a band gap value of 2.3 eV. Such value is confirmed by the band structure diagrams. The obtained band gap value of 2.3 eV, when doping 5% of sulfur in this work is an agreement when doping ZrO2 with experimental studies. We also deduce the band gap value 1.2 eV when doping this material with 9% of sulfur.

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