Optical and dielectric properties of $\beta$-$\text{Ta}_2\text{O}_5$

C. Valencia-Balvín$^1$, S. Orozco$^2$, J. M. Osorio-Guillén$^3$, S. Pérez-Walton$^1$

$^1$ Facultad de Ingeniería, Instituto Tecnológico Metropolitano ITM, Calle 73 No 76A–354 Vía al Volador, Medellín, Colombia
$^2$ Facultad de Ciencias Exactas y Aplicadas, Instituto Tecnológico Metropolitano ITM, Calle 73 No 76A–354 Vía al Volador, Medellín, Colombia
$^3$ Instituto de Física, Universidad de Antioquia UdeA, Calle 70 No 52–21, Medellín, Colombia

E-mail: camilovalencia@itm.edu.co

Abstract. Tantalia ($\text{Ta}_2\text{O}_5$) is an interesting material which is used in several technological applications. In particular, this wide gap semiconductor is used as a new material for memristive devices, which could provide a paradigm shift on the memory devices fabrication. These new devices would be faster, denser and less power consuming than those available today. Because of this, we present a study of the optical and dielectric properties of $\beta$-$\text{Ta}_2\text{O}_5$ polymorph by means of first-principles Density Functional Theory calculations. Taking as a starting point the Nashed’s model of the crystal structure of $\beta$-$\text{Ta}_2\text{O}_5$ and the generalized gradient approximation (GGA-PBEsol), we calculated the equation of state (EOS) of this polymorph. From EOS we identify the equilibrium volume and for this we calculated the frequency dependent dielectric tensor, refractive index ($n = 2.63$), absorption coefficient and transmittance. Also, we calculated the electronic ($\varepsilon_{\infty} = 6.98$) and ionic contribution ($\varepsilon_0 = 43.51$) to static dielectric constant and it was compared with some reported values in the literature.

1. Introduction

$\text{Ta}_2\text{O}_5$ is a wide gap semiconductor whose main characteristic is its high dielectric constant, which makes possible that this compound can be used in a variety of technological applications like memristor [1], anti-reflective films in solar cells [2] and water splitting processes [3]. For several years, numerous experimental studies have reported a set of polymorphs for $\text{Ta}_2\text{O}_5$, finding crystal structures at low and high temperature and high pressures. Mainly, at low temperature it has been reported an orthorhombic structure without oxygen vacancies, the $\beta$-phase, for which has been reported several experimental refinements [4]. Furthermore, for this structure has been proposed different theoretical models [5, 6, 7] to describe adequately the structural, electronic and optical properties of this phase. One such model is the one proposed by Nashed et al. [8], in which an orthorhombic structure described by the space group $Pmmm$ with two tantalum (Ta) and five oxygen (O) atoms in the unit cell is proposed, where local structures consist of chains of octahedral linked by the corners. In this work, we have taken this model as a reference to study the structural, electronic and optical properties of this compound in the $\beta$-phase and we had compared our results with existing experimental data and theoretical results obtained in other studies.
2. Simulation details
In this study, we have calculated the total energy as a function of the unit cell volume \( E=E(\Omega) \), by fully relaxing the ionic positions and the shape of the unit cell for each calculated volume. Then, the obtained energies were fitted to a polynomial Eulerian strain Birch-Murnaghan equation of state (EOS) of order 4 \([9, 10]\), where we extracted the equilibrium volume \( \Omega_0 \). All total energies, ionic forces and stress tensor components have been calculated via Density Functional Theory (DFT), where we have used for the exchange-correlation functional the generalized gradient approximation (GGA) with the PBEsol parameterization \([11]\). To solve the Kohn-Sham equations, we have used the projector augmented wave (PAW) method \([12]\) as implemented in the VASP code \([13, 14]\). The PAW atomic reference configurations are: \( 5p^6 \ 5d^4 \ 6s^1 \) for Ta and \( 2s^2 \ 2p^4 \) for O, where only electrons treated as valence electrons are explicitly enumerated. The energy cut-off in the planes waves expansion is 520 eV. Brillouin-zone integration has been performed on a Monkhorst-Pack \( 4 \times 8 \times 8 \) k-mesh with a Gaussian broadening of 0.01 eV for relaxation (ionic forces are converged to 0.1 meV/\( \text{Å} \)) and a \( \Gamma \)-centered \( 4 \times 8 \times 8 \) k-mesh using the tetrahedron method including Blöchl corrections \([15]\) for the calculation of the total energy, the charge density and the optical properties. Furthermore, for electronic structure calculation we have also used the HSE06 hybrid functional \([16, 17]\), which permitted us to obtain a better gap estimation. The calculation of the optical properties associated with the interband transitions are done by means of the imaginary part of the frequency dependent dielectric tensor \( \varepsilon^{(2)}(\vec{q}, \omega) \) in the long-wavelength limit \( \vec{q} \rightarrow 0 \), using the methodology developed for the PAW method \([18]\). The real part of the frequency dependent dielectric tensor is obtained from the imaginary part through the Kramers-Kröning relationship. From the knowledge of the dielectric tensor, we have calculated the refractive index \( n(\omega) \), the extinction coefficient \( \kappa(\omega) \), the absorption coefficient \( \alpha(\omega) \) and the transmittance, using explicitly the equations listed in the reference \([19]\). Finally, we have also calculated the low-frequency dielectric tensor \( \varepsilon_0 \) through density functional perturbation theory \([20]\).

3. Results
3.1. Crystal structure
The crystal structure of \( \beta-\text{Ta}_2\text{O}_5 \) is formed from a set of \( \text{TaO}_6 \) octahedra where the Ta atom is in the octahedron center and O atoms are at the corners, where there is a re-orienting of the conventional structure \([4]\) of \( \beta-\text{Ta}_2\text{O}_5 \) such that the \( b \)-vector becomes along the \( z \)-axis and the \( c \)-vector is in the \( x-y \) plane \([8]\), halving the number of atoms in the unit cell. In this new model the octahedral share corners as well (Figure 1).

Figure 1. Calculated equilibrium crystal structure of \( \beta-\text{Ta}_2\text{O}_5 \). Ta and O atoms are represented by green and blue spheres, respectively.

In this model, \( \beta-\text{Ta}_2\text{O}_5 \) is an orthorhombic structure described by the space group \( Pmmm \), with one formula unit per unit cell where two Ta ions are located at the Wyckoff positions: \( 1a \)
(Ta$_1$) and 1$f$ (Ta$_2$), while five O ions are distributed over the four Wyckoff positions: 1$c$ (O$_1$), 2$i$ (O$_2$), 1$e$ (O$_3$) and 1$h$ (O$_4$). In addition, we have found that the orthorhombic lattice has been conserved during the stress tensor optimization (unit cell vectors relaxation) for all the fixed volumes, there is no tilting on any direction ($\angle$ O-Ta-O = 180°) and all Ta ions remain at the center of the octahedral.

3.2. Equation of state
The equation of state for $\beta$-Ta$_2$O$_5$ was obtained fitting the energies as a function to volume using the Birch-Murnaghan strain curve given by a fourth-order Eulerian polynomial, where the EOS is shown in the Figure 2. From EOS, we obtained the equilibrium geometry with a lattice parameters $a = 6.4489$ Å, $b = 3.6753$ Å and $c = 3.8670$ Å, values which are in good agreement with the parameters reported in the references [8] and they are comparable with values reported for low-temperature Ta$_2$O$_5$ structure [21], when the standard $\beta$-Ta$_2$O$_5$ is reconstructed from our calculated structure using a $1 \times 2 \times 1$ supercell.

![Figure 2. Calculated total energy per atom versus volume per atom for $\beta$-Ta$_2$O$_5$. GGA-PBEsol total energies (denoted by the filled symbols) are fitted using the methodology described in [9, 10].](image)

For this structure, the cohesive energy is calculated using the equation:

$$E_c = \frac{(E_{\beta-Ta_2O_5}^{\text{bulk}})}{n} - \frac{(pE_{\text{Ta}^{\text{atom}}} + qE_{\text{O}^{\text{atom}}})}{n},$$

where $E_c$ is the cohesive energy, $n$ is the total number of atoms, $p$ and $q$ are the number of Ta and O atoms, respectively. In this case, we obtained a value of -7.34 eV, which at being compared with the theoretical value reported by Wu et al. [22], we find that there is a relative error of 1%, evidencing that our estimate for the equilibrium geometry is good agreement with the Wu et al. calculation.

3.3. Electronic structure
The calculated dispersion relation for $\beta$-Ta$_2$O$_5$ is presented in Figure 3. The dispersion relation shows that $\beta$ phase is an indirect wide gap semiconductor. The calculated energy gap with
PBEsol (HSE06) is 0.25 eV (1.54 eV), which we have compared with the experimental value of the gap for the orthorhombic low-temperature phase and others reported theoretical values in the Table 1. In this table, we can see that the calculated gap with HSE06 is in good agreement with calculated bandgap with other works for $\beta$-Ta$_2$O$_5$. Furthermore, we found that the valence band maximum (VBM) and the conduction band minimum (CBM) are located at $R = (1/2, 1/2, 1/2)$ and $Y = (0, 1/2, 0)$, respectively; as it can be observed in Figure 3.

Table 1. Calculated indirect and direct gaps for $\beta$-Ta$_2$O$_5$.

| Functional | $\Delta E$ (eV) | $\Gamma$ | $X$ | $R$ | $T$ | Reference |
|------------|-----------------|----------|-----|-----|-----|-----------|
| PBEsol$^*$ | 0.25            | 1.06     | 1.52| 0.8 | 0.44| This work. |
| PBE$^*$    | 1.45            |          |     |     |     | [8]       |
| PBE$^\dagger$ | 0.230         |          |     |     |     | [23]      |
| HSE06$^*$ | 1.54            | 2.61     | 2.94| 2.36| 1.96| This work. |
| HSE06$^\dagger$ | 0.9          |          |     |     |     | [22]      |

$^*$ Nashed et al model  
$^\dagger$ Aleshina et al. structure

Figure 3. Band structure for $\beta$-Ta$_2$O$_5$ calculated with GGA-PBEsol and HSE06 functionals. The blue points represent GGA-PBEsol calculation and red points, represent HSE06 calculation.

A detailed analysis of the dispersion relation allows us to identify that the valence band is the result of the hybridization of O $p$-states and Ta $d$-states, and the conduction band is constructed
mainly of Ta $d$-states and a small contribution of O $p$-states, where the character of the VBM is dominated by O $p$-states, whereas the CBM is dominate by Ta $d$-states. In the case of VBM, contributions are distributed as follows: O$_1$ $p_y$-states and O$_3$ $p_z$-states, while in the CBM the distribution of states is Ta$_2$ $d_{xz}$-states. Additionally, we can observe that HSE06 calculation produce a rigid shift of the conduction band (CB) to higher energies respect to VBM, where the topology of bands is basically the same.

3.4. Dielectric tensor

In the case of an orthorhombic crystal, the dielectric tensor has three components different from zero: the three components of the diagonal ($\varepsilon_{xx}$, $\varepsilon_{yy}$ and $\varepsilon_{zz}$). In the Figure 4 (a-c), we show the calculated diagonal components for imaginary part of dielectric tensor $\varepsilon^{(2)}_{\alpha\beta}$ of $\beta$-Ta$_2$O$_5$ with PBEsol and HSE06 functionals. In this case, the dielectric tensor is anisotropic as it can be observed from the position of the main absorption peaks among its components, which are slightly located at different energies. The directional average of $\varepsilon^{(2)}_{\alpha\beta}$ with PBEsol (HSE06) shows the main peaks located at 4.1, 4.6, 6.5 and 9.4 eV (5.7, 6.1, 7.3 and 11.5 eV). These peaks are associated to interband transitions between O $p$-states in the valence band and Ta $d$-states in the conduction band.

**Figure 4.** Imaginary (a), (b) and (c)) and real (d), e) and f)) parts of dielectric tensor for $\beta$-Ta$_2$O$_5$.

In Table 2, we show the calculated electronic ($\varepsilon_{\infty}$) and ionic contribution ($\varepsilon_{0}$) to static dielectric tensor. Here, we can observe that $\varepsilon_{\infty}$ presents some anisotropy, where $\varepsilon_{xx}$ is lower than the other diagonal components $\varepsilon_{yy}$ and $\varepsilon_{zz}$. On the other hand, $\varepsilon_{0}$ presents a high degree of anisotropy; the component $\varepsilon_{zz}$ is much larger than $\varepsilon_{xx}$ and $\varepsilon_{yy}$. Furthermore, $\varepsilon_{yy}$ is approximately 1.8 times $\varepsilon_{xx}$. Finally, we have also calculated the directional average static
dielectric constant ($\varepsilon(0) = \varepsilon_\infty + \varepsilon_0$), where $\varepsilon_\infty$ and $\varepsilon_0$ are the directional averages of the electronic and ionic contribution to static dielectric tensor. These average values with PBEsol (HSE06) are $\varepsilon_\infty = 6.98$ (4.0) and $\varepsilon_0 = 43.51$, which permit us to obtain $\varepsilon(0) = 50.5$ with PBEsol functional. We have compared our results with the values reported in reference [25], finding relative errors around of 15% and 17%, respectively. These results show that our calculations are in agreement with the values reported in that study.

| $\varepsilon_\infty$ | $\varepsilon_0$ |
|---------------------|-----------------|
| \begin{pmatrix} 5.54 & 0.00 & 0.00 \\ 0.00 & 7.27 & 0.00 \\ 0.00 & 0.00 & 8.13 \end{pmatrix} | \begin{pmatrix} 6.44 & 0.00 & 0.00 \\ 0.00 & 11.33 & 0.00 \\ 0.00 & 0.00 & 112.77 \end{pmatrix} |

3.5. Optical properties

Once calculated the dielectric tensor along the three Cartesian directions, we have proceeded to calculate the generalized refractive index. The Figure 5-(a) correspond to the refractive index $n$, whereas the Figure 5-(b) correspond to the extinction coefficient $\kappa$. We can observe that the calculated PBEsol (HSE06) value of $n$ at low-frequencies is 2.63 (2.2). For $\beta$-Ta$_2$O$_5$ we have not found in the literature a reported experimental value for $n$, but the reported value for an ultra-thin film of Ta$_2$O$_5$ is 2.15 [26], which compares well to our calculated values. In the Figure 5-(b), we can observe that the maximum absorption peaks are localized at 4.7, 6.2 and 9.9 eV (6.3, 7.2, 8.4 and 11.6 eV) with PBEsol (HSE06). These values are associated with inter-band transitions between O $p$-states in the valence band and Ta $d$-states in the conduction band.

After the calculation of the refractive index, also we have obtained the transmittance (Figure 6-(a)). We can observe that in the visible region (between 0.1 $\mu$m and 1 $\mu$m), the behavior of the transmittance is constant, with a value of 79% (85%) with PBEsol (HSE06), a result which indicates that in the visible region this material in $\beta$-phase is almost transparent. Finally, we calculated the absorption coefficient $\alpha$ which we show in the Figure 6-(b). This calculation shows that the absorption is nearly none in the visible region (around 2-3 eV), which confirms that this region $\beta$-Ta$_2$O$_5$ is transparent material and the first absorption peak is located in the middle ultraviolet region. Additionally, we observed the steepest increase with PBEsol (HSE06) of around 1.56 eV (2.83 eV), a value that is associated with the optical gap and it is consistent with our calculation.

4. Conclusions

In this paper we have studied the crystal and electronic structure and dielectric and optical properties of $\beta$-Ta$_2$O$_5$. We have identified that the valence band is a hybridization of O $p$ and Ta $d$-states, while the conduction band is mainly form for Ta $d$-states. Further, this semiconductor in this phase presents an indirect gap, where the VBM and CBM is located in the points $R = (1/2, 1/2, 1/2)$ and $Y = (0, 1/2, 0)$, respectively. Also, we have calculated the static dielectric constant ($\varepsilon(0) = 50.5$), value which is in good agreement with values reported in others experimental and theoretical works. Finally, we have calculated the transmittance and absorption coefficient. Of this calculation we have identified that in the visible region tantalum in this phase is a transparent material.
Figure 5.  a) Refractive index $n$ and b) extinction coefficient $\kappa$.

Figure 6. Transmittance and absorption coefficient ($\alpha$).

Acknowledgments
This work was supported by Centro de Investigaciones–Instituto Tecnológico Metropolitano (Colombia) and CIEN–CODI–Vicerrectoría de Investigación–Universidad de Antioquia (Estrategia de Sostenibilidad 2016–2017).
References

[1] Lee M J, Lee C B, Lee D, Lee S R, Chang M, Hur J H, Kim Y B, Kim C J, Seo D H, Seo S, Chung U I, Yoo I K and Kim K 2011 Nature Materials 10 625
[2] Kumar K J, Raju N and Subrahmanyan A 2011 Surf. Coat. Technol. 205 S261–S264
[3] Sato S, Morikawa T, Saeki S, Kajino T and Motohiro T 2010 Angewandte Chemie International Edition 49 5101–5105
[4] Aleshina L and Loginova S V 2002 Crystallogr. Rep. 47 415–419
[5] Ramprasad R 2003 J. Appl. Phys. 94 5609–5612
[6] Lee S H, Kim J, Kim S J, Kim S and Park G S 2013 Phys. Rev. Lett. 110 235502
[7] Andreoni W and Pignedoli C A 2010 Appl. Phys. Lett. 96 062901
[8] Nashed R, Hassan W M I, Ismail Y and Allam N K 2013 Phys. Chem. Chem. Phys. 15 1352–1357
[9] de-la Roza A O and Luana V 2011 Comput. Phys. Commun. 182 1708–1720
[10] de-la Roza A O, Abbasi-Perez D and Luana V 2011 Comput. Phys. Commun. 182 2232–2248
[11] Perdew J P, Ružańska A, Csonka G I, Vydrov O A, Scuseria G E, Constantin L A, Zhou X and Burke K 2008 Phys. Rev. Lett. 100 136406
[12] Blöchl P 1994 Phys. Rev. B 50 17953–17979
[13] Kresse G and Furthmüller J 1996 Phys. Rev. B 54 11169–11186
[14] Kresse G and Joubert D 1999 Phys. Rev. B 59 1758–1775
[15] P E B, Jepsen O and Andersen O K 1994 Phys. Rev. B 49 16223–16233
[16] Heyd J, Scuseria G E and Ernzerhof M 2003 J. Chem. Phys. 118 8207–8215
[17] Heyd J, Scuseria G E and Ernzerhof M 2006 J. Chem. Phys. 124 219906
[18] Gajdos M, Hummer K, Kresse G, Furthmüller J and Bechstedt F 2006 Phys. Rev. B 73 045112
[19] Pérez-Walton S, Valencia-Balvín C, Dalpian G and Osorio-Guillén J 2013 Phys. Status Solidi B 250 1644—1650
[20] Giannozzi P and Baroni S 2005 Handbook of Materials Modeling 189–208
[21] Fukunoto A and Miwa K 1997 Phys. Rev. B 55 11155–11160
[22] Wu Y N, Li L and Cheng H P 2011 Phys. Rev. B 83 144105
[23] Sahu B R and Kleinman L 2004 Phys. Rev. B 69 165202
[24] Gu T, Wang Z, Tada T and Watanabe S 2009 J. Appl. Phys. 106 103713
[25] Sergiu Clima G P, Elshocht S V, Gendt S D, Heyns M M, Wouters D J and Kittl J A 2009 ECS Trans. 19 729–737
[26] Zhang D X, Zheng Y X, Cai Q Y, Lin W, Wu K N, Mao P H, Zhang R J, Zhao H B and Chen L Y 2012 Appl. Phys. A 108 975–979