

Proceeding Paper

# First Principles Study on the Features of $\text{Ca}_x\text{Sr}_{2-x}\text{Ta}_2\text{O}_7$ ( $x = 0, 1$ ) as a Photocatalytic Material <sup>†</sup>

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† Presented at the 3rd International Electronic Conference on Applied Sciences, 1–15 December 2022; Available online: <https://asec2022.sciforum.net/>.

**Abstract:** With hydrogen as one of the energetic vectors craved for use in the future, the successful de-carbonization of the energy sector will require an increase in hydrogen production from renewable resources. Materials that are able to catalyze the water-splitting reaction through sunlight absorption have been widely studied as an adequate solution for green hydrogen generation. Among the proposed tantalum-based oxide materials,  $\text{Sr}_2\text{Ta}_2\text{O}_7$  displays moderate photocatalytic activity. Aiming to improve the photocatalytic properties by means of compositional modifications, this work presents a DFT study of the Sr substitution with Ca. The structural, energetic, and electronic features of the phases of  $\text{Ca}_x\text{Sr}_{2-x}\text{Ta}_2\text{O}_7$  ( $0 < x < 1$ ) have been examined. The computational results utilizing the SCAN functional show that there is a slight decrement in the band gap value (from 3.65 eV for  $x = 0$  to 3.50 eV for  $x = 1$ ) concomitant to a minor distortion of the crystal structure.

**Keywords:**  $\text{Sr}_2\text{Ta}_2\text{O}_7$ ; green hydrogen; photocatalysis; water splitting; DFT



**Citation:** Gómez-Toledo, M.;

Boulahya, K.; Arroyo-de Dompablo,

M.E. First Principles Study on the Features of  $\text{Ca}_x\text{Sr}_{2-x}\text{Ta}_2\text{O}_7$  ( $x = 0, 1$ ) as a Photocatalytic Material. *Eng. Proc.* **2023**, *31*, 3. <https://doi.org/10.3390/ASEC2022-13794>

*Proc.* **2023**, *31*, 3. <https://doi.org/10.3390/ASEC2022-13794>

Academic Editor: Nunzio Cennamo

Published: 2 December 2022

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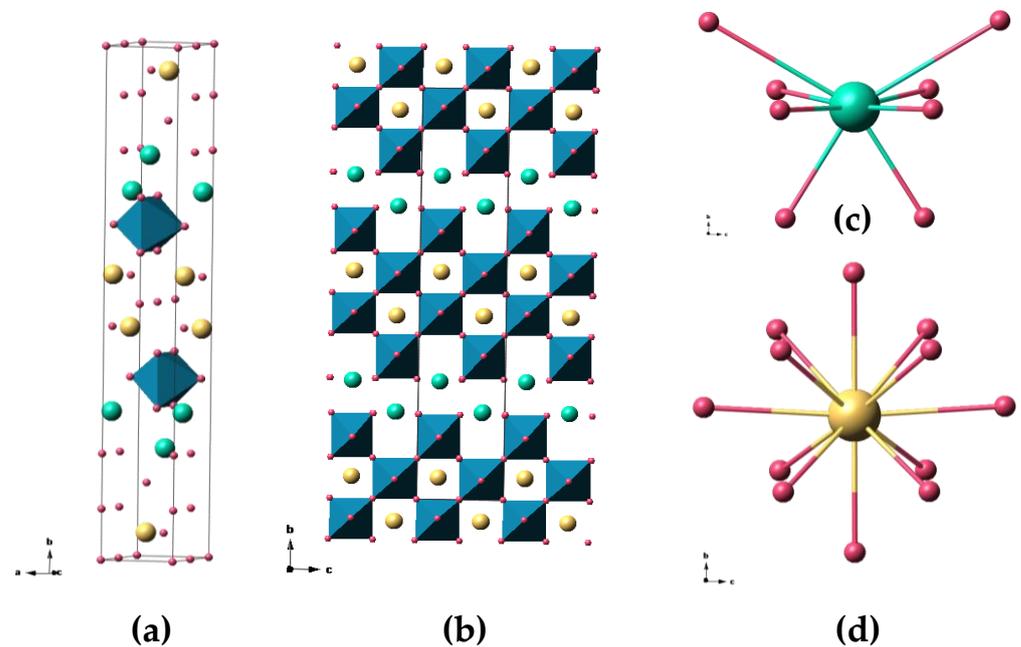
## 1. Introduction

Climate change might be one of the biggest challenges that we face nowadays as a society. Currently, most of the produced energy comes from fossil fuels, which contributes to greenhouse gas emissions. Energy production through renewable sources is being explored as a solution to this major issue. In that respect, hydrogen ( $\text{H}_2$ ) seems to be the energetic vector of the future [1,2]; it presents a high combustion efficiency and the highest energy content per unit mass of all fossil fuels normally used [3]. However, hydrogen production rarely comes from zero-emission sources. In this sense, hydrogen production through water splitting using sunlight (i.e., photocatalysis) presents a key to green hydrogen generation [4] (p. 3).

The photocatalytic dissociation of water can be achieved using semiconductor materials that are able to absorb sunlight, leading to the promotion of electrons from the valence band (VB) to the conduction band (CB). There are, however, some vital concerns that must be considered: the VB maximum should be below the  $\text{O}_2/\text{H}_2\text{O}$  oxidation potential (1.23 eV) and the CB minimum should be above the  $\text{H}_2\text{O}/\text{H}_2$  reduction potential (0.0 eV). Likewise, the band gap should be smaller than 3.0 eV to use visible light and larger than 1.23 eV to fulfill band position requirements [5]. Several compounds have been studied for this purpose, for example,  $\text{TiO}_2$ ,  $\text{WO}_3$ ,  $\text{CdSe}$ ,  $\text{CdS}$ , and  $\text{Ta}_2\text{O}_5$  [6]. Among the investigated  $d^0$ -TM oxides,  $\text{Sr}_2\text{Ta}_2\text{O}_7$  [7,8] shows some exciting characteristics, particularly in its CB position relative to  $\text{H}_2\text{O}/\text{H}_2$  reduction potential. However, its large band gap (4.6 eV) limits the light absorption to the UV region of sunlight.

The  $\text{Sr}_2\text{Ta}_2\text{O}_7$  compound presents a perovskite-derived structure [9], where four perovskite layers form 2D nets perpendicular to the  $c$  axis, as shown in Figure 1. In the  $\text{ABO}_3$  perovskite blocks, Ta occupies the B position, being coordinated to six O atoms. Sr occupies two different positions, Sr(1) and Sr(2), that are coordinated to 8 and 12 O atoms,

respectively. Sr(1) can be described as an atom between perovskite block layers, while Sr(2) can be seen as an atom inside those blocks.



**Figure 1.** (a) Crystallographic unit cell of Sr<sub>2</sub>Ta<sub>2</sub>O<sub>7</sub> [S.G. Cmc<sub>2</sub>m (No.63)]; (b) representation of the layered structure showing the perovskite blocks; (c) detail of the Sr(1) coordination environment; and (d) detail of Sr(2) coordination environment. Color code: Ta atoms are shown in blue, O in red, Sr(1) in green, and Sr(2) in yellow.

Previous computational studies [10,11] suggest that anion modifications along with cation doping in the Ta site tune the band gap value and the relative positions of the VB/CB, thereby influencing the photocatalytic activity. As for cation doping in the Sr site, some authors [12] have experimentally demonstrated that the partial substitution of Sr for Ba improves the photocatalytic activity. Specifically, the solid solution Sr<sub>2-x</sub>Ba<sub>x</sub>Ta<sub>2</sub>O<sub>7</sub> was successfully synthesized in the compositional range  $0 < x < 0.4$ , with the term  $x = 0.4$  displaying the best catalytic performance. This makes the investigation of the substitution of Sr with other cations such as Ca, appealing in that it could potentially enhance the photocatalytic activity of Sr<sub>2</sub>Ta<sub>2</sub>O<sub>7</sub>. For this purpose, this work focuses on the computational study through DFT calculations of the structural and electronic changes that the substitution of Sr with Ca can provoke in the Ca<sub>x</sub>Sr<sub>2-x</sub>Ta<sub>2</sub>O<sub>7</sub> family. In particular, the  $x = 0$  and 1 phases are studied.

## 2. Materials and Methods

### 2.1. Crystallographic Models

Crystallographic models were built from the Sr<sub>2</sub>Ta<sub>2</sub>O<sub>7</sub> structure (ICSD file 601) [9]. The structure was used to model the hypothetical Sr<sub>2-x</sub>Ca<sub>x</sub>Ta<sub>2</sub>O<sub>7</sub> compound with,  $x = 1$ . However, since there are two possible crystallographic sites for the Sr substitution (Figure 1), two models of CaSrTa<sub>2</sub>O<sub>7</sub> were constructed. The substitution of Sr(1) for Ca led to the model named CaSrTa<sub>2</sub>O<sub>7</sub>(1), and the substitution of Sr(2) for Ca generated the model named CaSrTa<sub>2</sub>O<sub>7</sub>(2).

### 2.2. Computational Methods

DFT calculations were performed using the VASP package (Vienna ab-initio simulation package) developed at the Universität Wien [13,14]. The Projector Augmented Wave (PAW) [15] method was used to describe the interaction of core electrons with nuclei, specifically  $4s^2 4p^6 5s^2$  for Sr,  $5p^6 6s^2 5d^3$  for Ta,  $2s^2 2p^4$  for O, and  $3s^2 3p^6 4s^2$  for Ca were

treated as valence electrons. A meta-GGA exchange-correlation functional was utilized; in particular, the recently developed strongly constrained and appropriately normed (SCAN) functional [16]. The energy cutoff was set at 600 eV throughout all calculations. Integration of the first Brillouin zone was carried out under the determination of k-points by the Monkhorst–Pack scheme. The k-point meshes were set at  $6 \times 2 \times 6$  in all cases, along with a Gaussian smearing parameter of 0.05 eV. For the density of states (DOS) calculations, the tetrahedron method with Bloch corrections [17] was employed. The tolerance threshold in total energy to achieve self-consistency was set at  $1 \times 10^{-4}$  eV. Structural relaxation was performed over atoms' position, as well as cell shape and volume. No symmetry constraints were imposed during a relaxation for the Ca models calculations.

### 3. Results and Discussion

#### 3.1. Crystal Structure

The structural optimization results for  $\text{Sr}_2\text{Ta}_2\text{O}_7$  within the SCAN functional are shown in Table 1. The lattice parameters obtained are in good agreement with experimental measurements [9], with errors below 0.5%. Likewise, distances results are, in general, in line with experimental values, showing deviations below 4.5%. Thus, the SCAN functional correctly reproduces the crystal structure of  $\text{Sr}_2\text{Ta}_2\text{O}_7$ .

**Table 1.** Lattice parameters and atomic distances in the  $\text{Sr}_2\text{Ta}_2\text{O}_7$  (S.G. Cmc<sub>2</sub>) structure and  $\text{CaSrTa}_2\text{O}_7$  models (S.G. Cmc<sub>2</sub>).

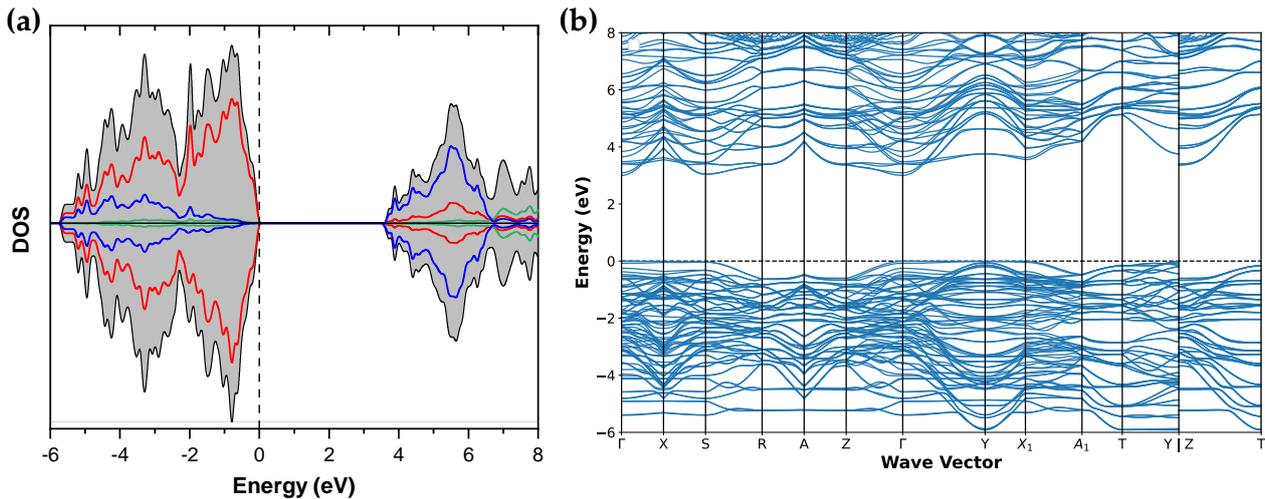
	Lattice Parameters (Å)				
	$\text{Sr}_2\text{Ta}_2\text{O}_7$			$\text{CaSrTa}_2\text{O}_7(1)$	$\text{CaSrTa}_2\text{O}_7(2)$
	Experimental	Calculated	% Error	Calculated	Calculated
a	3.9376	3.9537	0.4	3.9084	3.9273
b	27.1986	27.1894	0.03	27.0999	27.0855
c	5.6927	5.6951	0.04	5.6119	5.6646
Volume (Å <sup>3</sup> )	609.50	612.22	0.4	594.40	602.56
	Distances (Å)				
	$\text{Sr}_2\text{Ta}_2\text{O}_7$			$\text{CaSrTa}_2\text{O}_7(1)$	$\text{CaSrTa}_2\text{O}_7(2)$
	Experimental	Calculated	% Error	Calculated	Calculated
Sr1/Ca1-O	2.47 (x4)	2.480	0.4	2.416	2.469
Sr1/Ca1-O	2.60 (x2)	2.575	1.0	2.435	2.572
Sr1/Ca1-O	3.27 (x2)	3.313	1.3	3.338	3.347
Sr2/Ca2-O	2.71 (x4)	2.719	0.3	2.697	2.653
Sr2/Ca2-O	2.827 (x4)	2.837	0.4	2.809	2.848
Sr2/Ca2-O	2.85 (x2)	2.852	0.1	2.811	2.849
Sr2/Ca2-O	2.70	2.629	2.6	2.650	2.476
Sr2/Ca2-O	2.74	2.743	0.1	2.731	2.721
Ta1-O	1.87 (x2)	1.855	0.8	1.871	1.859
Ta1-O	1.979 (x2)	1.989	0.5	1.976	1.990
Ta1-O	2.16 (x2)	2.071	4.1	2.141	2.128
Ta2-O	1.89 (x2)	1.855	1.9	1.832	1.907
Ta2-O	1.98 (x2)	1.997	0.9	1.969	1.978
Ta2-O	2.07 (x2)	2.157	4.2	2.067	2.032

Regarding the relative stability of the two crystallographic models proposed for  $\text{CaSrTa}_2\text{O}_7$ , DFT calculations show that the  $\text{CaSrTa}_2\text{O}_7(1)$  model has lower energy than the  $\text{CaSrTa}_2\text{O}_7(2)$  model (energy difference of 332 meV). The relative stability can be rationalized considering the ionic radii of  $\text{Ca}^{2+}$  ( $r = 1.12$  Å for C.N. = 8 and  $1.34$  Å for C.N. = 12 [18]) and  $\text{Sr}^{2+}$  ( $r = 1.26$  Å for C.N. = 8 and  $1.44$  Å for C.N. = 12 [18]). This calculated energy indicates that a more stable structure is formed if the larger  $\text{Sr}^{2+}$  occupies the position inside perovskite blocks (C.N. = 12), which is to say, the smaller  $\text{Ca}^{2+}$  cation will tend to occupy the site between perovskite layers position (C.N. = 8).

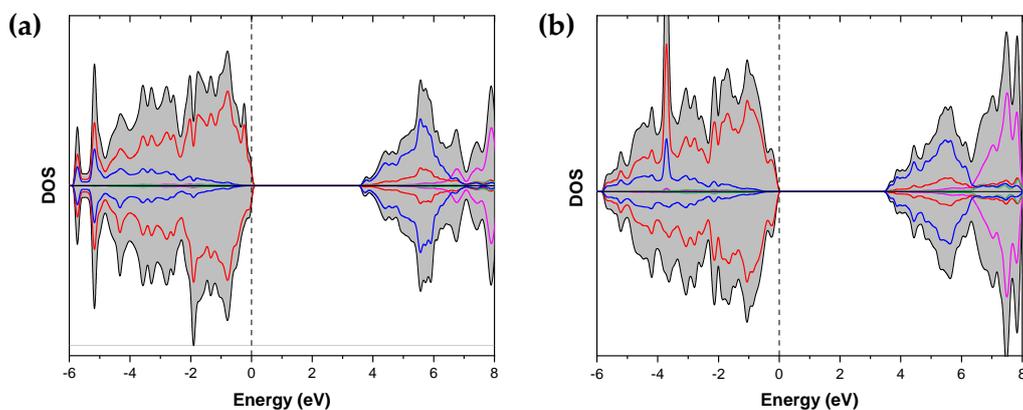
Lattice parameters and atomic distances for the most stable  $\text{CaSrTa}_2\text{O}_7$  model are listed in Table 1. As expected, the introduction of the smaller  $\text{Ca}^{2+}$  ion produces a contraction of the unit cell and a reduction in all lattice parameters. Overall, the introduction of Ca ions preserves the initial crystal structure of  $\text{Sr}_2\text{Ta}_2\text{O}_7$ .

### 3.2. Electronic Structure

Figures 2 and 3 show the calculated density of states and band structure of the  $\text{Sr}_2\text{Ta}_2\text{O}_7$  and DOS of the two  $\text{CaSrTa}_2\text{O}_7$  models, respectively.



**Figure 2.** (a) Calculated density of states of  $\text{Sr}_2\text{Ta}_2\text{O}_7$ . (b) Calculated band structure of  $\text{Sr}_2\text{Ta}_2\text{O}_7$ . The Fermi level is set at the zero of energy. Color code: total black, O red, Sr green, and Ta blue.



**Figure 3.** Calculated density of states of (a)  $\text{CaSrTa}_2\text{O}_7(1)$  and (b)  $\text{CaSrTa}_2\text{O}_7(2)$ . The Fermi level is set at the zero of energy. Color code: total black, O red, Sr green, Ca pink, Ta blue.

The DOS for  $\text{Sr}_2\text{Ta}_2\text{O}_7$  is represented in Figure 2a. The Fermi level is set at the 0 of energy. The VB is mainly formed by the  $2p$  states of O while CB is composed of the  $5d$  Ta empty states (in blue). Yet, a good hybridization, signature of Ta-O covalence, exists between O and Ta states in both bands. Sr barely contributes to forming the valence and conduction bands. As shown in Figure 2a,b, band gap of 3.65 eV is obtained using the SCAN functional. This result deviates from the experimental one (4.6 eV), given that band gap underestimation is a known failure of DFT methods [19].

Despite the limitations of DFT to reproduce accurate band-gap values, the trends in band-gaps due to chemical composition modifications are fully reliable [11].

Figure 3 shows the calculated DOS for the two models used to simulate the  $\text{CaSrTa}_2\text{O}_7$  compounds.  $\text{CaSrTa}_2\text{O}_7(1)$  has a band gap of 3.55 eV while the  $\text{CaSrTa}_2\text{O}_7(2)$  band gap is

3.50 eV. Therefore, calculations suggest that in the  $\text{Sr}_{2-x}\text{Ca}_x\text{Ta}_2\text{O}_7$  family, the trend is to reduce the band gap as  $x$  increases. Importantly, band gap variations are of only about 0.15 eV when going from  $x = 0$  to  $x = 1$ . It is well documented that in  $d^0$  transition metals oxides crystallizing in the  $\text{ABO}_3$  perovskite structure, the A substitution with other ions can provoke a distortion in the crystal structure, which could ultimately affect the electronic structure producing significant band-gap values modifications [20]. Since, in the present case, the partial substitution of Sr with Ca causes minor crystal structure modifications, the variations in the electronic structure are subtle. Additionally, valence and conduction bands in  $\text{CaSrTa}_2\text{O}_7$  models have essentially the same features as in the  $\text{Sr}_2\text{Ta}_2\text{O}_7$  phase.

Considering the exposed results, the substitution of Sr with Ca in  $\text{Sr}_2\text{Ta}_2\text{O}_7$  only leads to a slight reduction in the band gap value that is independent of the Ca position. This seems insufficient to cause an effective change in the photocatalytic activity of the material. Taking into account the experimentally observed improvement of photocatalytic activity when substituting Sr with Ba in some  $\text{Sr}_{2-x}\text{Ba}_x\text{Ta}_2\text{O}_7$  phases [12], more work is needed to assess the impact of the Sr substitution in  $\text{Sr}_2\text{Ca}_2\text{O}_7$  with Ca/Ba and other cations in the electronic structure. It should be highlighted that other critical features could account for an improved catalytic activity in  $\text{Sr}_{2-x}\text{Ba}_x\text{Ta}_2\text{O}_7$ , such as the decrement of the electron-hole recombination.

#### 4. Conclusions

Computational investigations at the level of Density Functional Theory (DFT) permit the prediction of some basic and critical features in view of the photocatalytic activity of materials. In this work, DFT methods are used to predict the crystal and electronic structures of the potential photocatalyst  $\text{Sr}_{2-x}\text{Ca}_x\text{Ta}_2\text{O}_7$ . We found that the  $x = 1$  phases preserve the perovskite-related structure of the parent  $\text{Sr}_2\text{Ta}_2\text{O}_7$ . The calculated DOS shows a band narrowing of 0.10–0.15 eV because of the Sr substitution with Ca. With band gaps of  $\sim 4.5$  eV, sunlight absorption by the  $\text{SrCaTa}_2\text{O}_7$  photocatalyst is limited to the UV region. Work is in progress to investigate other substitutions that may enhance the photocatalytic activity of  $\text{Sr}_2\text{Ta}_2\text{O}_7$ .

**Author Contributions:** M.G.-T.: methodology, formal analysis, investigation, data curation, writing-original draft preparation, visualization. K.B.: conceptualization, validation, resources. M.E.A.-d.D.: conceptualization, supervision, project administration, funding acquisition. All authors have read and agreed to the published version of the manuscript.

**Funding:** Universidad Complutense de Madrid (FEI-EU-22-01-4129585) and Comunidad de Madrid (PEJ-2020-AI/IND-18065 under the program Ayudas para la contratación de Ayudantes de Investigación y Técnicos de Laboratorio).

**Institutional Review Board Statement:** Not applicable.

**Informed Consent Statement:** Not applicable.

**Data Availability Statement:** The data supporting the plots within this work and other findings of this study are available from the corresponding authors upon reasonable request.

**Acknowledgments:** Authors thank I. Collado and R. Carrasco for their contributions to the experimental data analysis.

**Conflicts of Interest:** The authors declare no conflict of interest.

#### References

1. Abdin, Z.; Zafaranloo, A.; Rafiee, A.; Mérida, W.; Lipiński, W.; Khalilpour, K.R. Hydrogen as an energy vector. *Renew. Sustain. Energy Rev.* **2020**, *120*, 109620. [[CrossRef](#)]
2. Dawood, F.; Anda, M.; Shafiullah, G.M. Hydrogen production for energy: An overview. *Int. J. Hydrog. Energy* **2020**, *45*, 3847–3869. [[CrossRef](#)]
3. Ishaq, H.; Dincer, I.; Crawford, C. A review on hydrogen production and utilization: Challenges and opportunities. *Int. J. Hydrog. Energy* **2022**, *47*, 26238–26264. [[CrossRef](#)]
4. Acar, C.; Dincer, I. Hydrogen Production. *Compr. Energy Syst.* **2018**, *3–5*, 1–40. [[CrossRef](#)]

5. Wang, Z.; Li, C.; Domen, K. Recent developments in heterogeneous photocatalysts for solar-driven overall water splitting. *Chem. Soc. Rev.* **2019**, *48*, 2109–2125. [[CrossRef](#)] [[PubMed](#)]
6. Osterloh, F.E. Inorganic materials as catalysts for photochemical splitting of water. *Chem. Mater.* **2008**, *20*, 35–54. [[CrossRef](#)]
7. Kato, H.; Kudo, A. New tantalate photocatalysts for water decomposition into H<sub>2</sub> and O<sub>2</sub>. *Chem. Phys. Lett.* **1998**, *295*, 487–492. [[CrossRef](#)]
8. Kudo, A.; Kato, H.; Nakagawa, S. Water Splitting into H<sub>2</sub> and O<sub>2</sub> on New Sr<sub>2</sub>M<sub>2</sub>O<sub>7</sub> (M = Nb and Ta) Photocatalysts with Layered Perovskite Structures: Factors Affecting the Photocatalytic Activity. *J. Phys. Chem. B* **2000**, *104*, 571–575. [[CrossRef](#)]
9. Ishizawa, N.M.F.; Kawamura, T.; Kimura, M. Compounds with Perovskite-Type Slabs. II. The Crystal Structure of Sr<sub>2</sub>Ta<sub>2</sub>O<sub>7</sub>. *Acta Crystallogr. Sect. B* **1976**, *B32*, 2564–2566. [[CrossRef](#)]
10. Liu, P.; Nisar, J.; Ahuja, R.; Pathak, B. Layered perovskite Sr<sub>2</sub>Ta<sub>2</sub>O<sub>7</sub> for visible light photocatalysis: A first principles study. *J. Phys. Chem. C* **2013**, *117*, 5043–5050. [[CrossRef](#)]
11. Peng, Y.; Ma, Z.; Hu, J.; Wu, K. A first-principles study of anionic (S) and cationic (V/Nb) doped Sr<sub>2</sub>Ta<sub>2</sub>O<sub>7</sub> for visible light photocatalysis. *RSC Adv.* **2017**, *7*, 40922–40928. [[CrossRef](#)]
12. Kim, K.Y.; Eun, T.H.; Lee, S.S.; Chon, U. Photocatalytic Activities and Structural Changes of Barium-Doped Strontium Tantalate. *Resour. Process.* **2009**, *56*, 138–144. [[CrossRef](#)]
13. Furthmüller, G.K.J. Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set. *Phys. Rev. B* **1996**, *54*, 11169. [[CrossRef](#)]
14. Kresse, G.; Joubert, D. From ultrasoft pseudopotentials to the projector augmented-wave method. *Phys. Rev. B* **1999**, *59*, 1758. [[CrossRef](#)]
15. Bloch, P.E. Projector augmented-wave method. *Phys. Rev. B* **1994**, *50*, 17953. [[CrossRef](#)] [[PubMed](#)]
16. Sun, J.; Ruzsinszky, A.; Perdew, J.P. Strongly Constrained and Appropriately Normed Semilocal Density Functional. *Phys. Rev. Lett.* **2015**, *115*, 036402. [[CrossRef](#)] [[PubMed](#)]
17. Blochl, P.E.; Jepsen, O.; Andersen, O.K. Improved Tetrahedron Method for Brillouin-Zone integrations. *Phys. Rev. B* **1994**, *49*, 16223–16233. [[CrossRef](#)] [[PubMed](#)]
18. Shannon, R.D. Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides. *Acta Crystallogr. A* **1976**, *32*, 751. [[CrossRef](#)]
19. Borlido, P.; Schmidt, J.; Huran, A.W.; Tran, F.; Marques, M.A.L.; Botti, S. Exchange-correlation functionals for band gaps of solids: Benchmark, reparametrization and machine learning. *NPJ Comput. Mater.* **2020**, *6*, 96. [[CrossRef](#)]
20. Eng, H.W.; Barnes, P.W.; Auer, B.M.; Woodward, P.M. Investigations of the electronic structure of d<sup>0</sup> transition metal oxides belonging to the perovskite family. *J. Solid State Chem.* **2003**, *175*, 94–109. [[CrossRef](#)]