AX₂-TYPE OF COMPOUNDS AND AN OVERVIEW OF THEORETICALLY INVESTIGATED TiO₂

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Abstract: AX₂-type compounds can be ionic, covalent or molecular types of structure, which depends on the size of atoms and the polarization properties. The materials of such type of the structure have different properties that can find the application in various areas of science and industry. Titanium dioxide, as a material of AX₂-type of the structure is a wide band gap semiconductor that has been widely investigated due to its photocatalytic properties and applicability for various purposes, such as the production of solar cells, decontamination of pollutants, elimination of microorganisms, suppression of cancer cells, etc. Experimental and theoretical studies of this metal oxide can give different data on the stability of individual crystalline modifications and their transitions. This study has presented an overview of theoretically examined TiO₂ modifications and current problems that can be encountered (such as various band gap values obtained by different methods and functionals; the difference between the stability of modifications examined on *ab initio* level and experimentally; the character of chemical bonds and transitions at the specific temperature and pressure conditions...) and overrun by optimal corrections added in calculations.

Keywords: AX₂-type compounds, TiO₂, *ab initio*, theoretical calculations

Introduction

The importance of researching the crystalline oxide structures of formula AX₂ is reflected in different properties that such a structure provides and thus finds the application in various areas of science and industry. This work will present the AX₂ type of structure and an overview of the theoretically examined AX₂ type compound - TiO₂ and its various crystal modifications. Titanium oxides build inorganic compounds titanates [1] which are white in color, insoluble in water and diamagnetic. In recent years, the semiconducting material Ti (IV) oxide, which has a large number of polymorphic phases over a wide range of pressures and temperatures, has received particular attention [2]. Pristine TiO₂ does not absorb in the visible part of the spectrum, it is stable in the dark, and after exposing to light it shows the photoactivity. It was discovered in the 1930s and has been used as a white pigment and in bleaching under different conditions [3,4]. In later years, it has proved to be a photocatalyst, and nowadays it is used in environmental protection, water and air purification, as well as in disinfection, or as a microbiocidal agent for certain strains of bacteria [3-5]. Recent studies have shown that through various morphological changes in structure or by doping, TiO₂ has been successfully demonstrated as a drug-delivery system and in the destruction of various tumor cells, *in vitro* and *in vivo* [6,7]. Also, it has been successfully used for years both as a diagnostic tool in medicine and in

the development of new types of implants [8,9]. Although the system has already been extensively tested, different theoretical and experimental approaches may provide new information on stable and metastable structures, as well as their properties and potential applications.

AX₂-Type Compounds

Compounds of the general chemical formula AX₂ can be ionic, covalent or molecular structures, which depends on the size of the atom and the polarization properties of the atoms that build it [10]. They can be formed by three types of cations originating from precious gas configurations of ions - which build ion crystals with relatively large ionic radii; cations with complete 18-electron configuration - which form covalent or semi-ionic bonds; and transition metal cations - which crystallize in structures similar to NiAs [10]. The power of polarization depends on the type of a cation. Small cations such as Be²⁺, Al³⁺, Si⁴⁺ have a great polarization power. Transition metal cations and cations with 18-electron configuration: Cu⁺, Au⁺, Ag⁺, Zn²⁺, Cd²⁺ and Hg²⁺, have higher polarization power than cations with noble gas configuration [11]. A and X can be the building blocks that build crystal lattices of CaF₂, TiO₂, CdI₂, MoS₂, CdCl₂ type structures [10]. Ion radius and polarization growth can be related, and also the transitions of these structures can be predicted in this way (it is

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shown graphically in Figure 1) [10-12].

Figure 1. Relation between ionic radii and ionic polarization in crystal structures of AX_2 -type compounds [10-12].

Figure 1 shows that with a decrease in radius, a transition from the fluoride-type structure to the TiO_2 rutile type of structure occurs. With a decrease in radius and an increase in polarization, a transition into the CdI_2 , MoS_2 , $CdCl_2$ types of structures occurs and still to the lattices of molecular type. Rutile can make a transition to the SiO_2 -type structure or to CdI_2 , MoS_2 , $CdCl_2$ structures with decreasing ionic radius ratios. Compounds CaF_2 , UO_2 , and ThO_2 of AX_2 -fluoride type structure have a coordination number for the cation $KB_{cat} = 8$ and a coordination number for the anion $KB_{ani} = 4$. A transition from fluoride to the rutile type changes the coordination number, so it becomes $KB_{cat} = 6$ for the cation. This transition occurs when the critical $R_A:R_X$ ratio of 0.73 is reached. The Coulomb energy is lower for the fluoride type than for the rutile type, indicating that all AX_2 ionic structures should crystallize as fluoride. When the ratio $R_A:R_X$ reaches a value lower than 0.41, the rutile type of the structure turns into SiO_2 type, and the cation coordination number becomes 4. None of the possible SiO_2 structures with large oxygen anions has a dense pack; high-temperature structures such as tridymite and cristobalite have an open structure; while quartz, which is stable at standard temperatures, has a slightly denser structure. With a further increase in the polarization effect, the structure of the rutile type can transform into the so-called "layered structure" characteristic for CdI_2 , MoS_2 and $CdCl_2$ structure types. Which structure will make a transition depends on many factors that cannot be precisely predicted. The layered structure actually represents the occupation of the structure with the distribution of opposite ionic charges in the horizontal layers, which generate positive and negative sequences [10,11]. Nowadays, various methods are successfully used for the structure prediction of the AX_2 type of chemical compounds such as the global exploration of the chemical system's energy landscapes [13,14], as well as the data mining searches in different databases [15-17].

Titanium Dioxide

The most thermodynamically stable modification of titanium dioxide is tetragonal rutile, but by heating at the elevated temperatures, metastable tetragonal anatase and metastable orthorhombic brookite irreversibly transit to rutile [3]. The experimentally obtained values of the band gap for the most interesting polymorphic phases of TiO_2 are: rutile, $P42/mnm$ (3.02 eV) and anatase, $I41/amd$ (3.2 eV) [18-20]. Apart from the aforementioned well-known structures, there are modifications that can be found in nature, simulated theoretically and obtained experimentally under certain conditions with the following space groups: $Pbca$ (brookite), $P121m1$, $C12m1$, $P121c1$, $P3121$, $Pa-3$, $Fm-3m$, $Pbcn$ (columbite), $P-62m$, $Pnma/Pbnm$ (cotunite), $P21/c$ (baddeleyite). Their structural parameters obtained experimentally or theoretically can be found in ICSD (Inorganic Crystal Structure Database) [21,22].

According to Ewald and Herman's crystal structure, the rutile type is known as the $C4$ ionic structure of the AX_2 group [11]. The rutile type structure is an octahedral structure, with the coordination number 6 – six oxygen surrounds titanium in the octahedron. The ratio of radius $R_A:R_X$ for ionic structures of the type AX_2 is in the range 0.41–0.73, while it is 0.49 for TiO_2 . The Ti^{4+} cation has a slightly deformed octahedral coordination. The structure is complex so that the Ti^{4+} ions are located at the corners and the center of the tetragonal unit cell, and the oxygen ions alternate in the diagonals of $c/2$ spacing, producing oxygen octahedral arrays joining the corners. MnO_2 , PbO_2 , SnO_2 oxides also belong to this type of the structure [11].

The crystalline structures of titanium (IV) oxide are most commonly represented as disordered TiO_6 octahedral blocks [3,23]. Rutile has a deformed structure and is stable at temperatures up to 700 °C and at the pressures up to 60 kbar, while anatase and brookite can be transformed into a rutile phase when the particles reach a certain size. Anatase has a tetragonal structure and slightly more deformed TiO_6 octahedron than rutile. Brookite has an orthorhombic, the most complicated crystal structure of these three phases, whose unit cell is composed of 8 TiO_6 octahedrons interconnected by the edges of the octahedron [11,23].

The structures of the unit cells of rutile, anatase and brookite are presented in Figure 2, visualized in the VESTA program [24] based on experimental data found in the ICSD database [16,17].

Figure 2. Unit cells of different TiO₂ crystalline modifications. An arrangement of TiO₆ octahedra in a) anatase unit cell; b) rutile unit cell; c) brookite unit cell [16,17,24].

Potential Application of TiO₂ in Nowadays

The presence of dyes from the textile industry in wastewater has proven to be the most common problem today in the ecosphere [3]. Photocatalysis is one of the recent successful treatments for removing such and similar pollutants from water. TiO₂, as a well-known photocatalyst, has played a major role in addressing this issue as highly active and stable over a wide range of operating conditions being economical, and more importantly, chemically and biologically inert, non-toxic and non-corrosive. The desirable products of photocatalytic degradation by TiO₂ are CO₂ and H₂O or safe inorganic anions and mineralization of various organic and inorganic pollutants in the environment. It is successfully

used for the oxidation of soil and surface water pollutants of organochloride and perchloroethylene [20]. Under the influence of UV radiation, TiO₂ can be used for a successful removal of toxic metal ions such as: Hg (II), Pb (II), Cd (II), Ag (I), Ni (II) and Cr (VI) [20,25]. Also, other metal ions such as Pt, Au, Cu and Fe ions can be reduced from aqueous solutions [25,26]. It has proven to be effective in photocatalytic decomposition reactions of various chemicals used in agriculture, such as pesticides, fungicides and herbicides [27].

Many research works [6-9,25-29] provide information on the properties of titanium dioxide particles that have biocidal effects and an influence on biomolecules and microorganisms such as Coenzyme A, *Lactobacillus acidophilus*, *Saccharomyces cerevisiae* and *Escherichia coli* cells, *Streptococcus sobrinus*, *Pseudomonas aeruginosa* protein and *Candida albicans*, after about 2 hours of exposure under the xenon or halogen lamp [20,25-29].

The photocatalytic action is based on the destruction of the cell wall of the microorganism, followed by the damage to the cell membrane and organelles. Some studies have shown that TiO₂ particles in the dark have an effect on the bacterial cell membrane, through direct contact, thereby damaging the outer membrane and liposaccharides of the bacterium [20]. Under the UV radiation, titanium dioxide nanoparticles have a fatal effect on germs, which is also applicable in sterile operating room blocks. Recently, more attention is being paid to improving the properties of TiO₂ that can be applied in the production and design of solar cells, as well as in the development of electrical devices [30,31].

An Overview of Theoretically Investigated TiO₂

Theoretical investigations support experimental data and have an important role in obtaining general conclusions about the examined system. Computational chemistry does not provide exact solutions (except in a few cases) but use approximate methods and give approximate solutions. The most commonly used quantum chemical methods in order to describe large systems are the Hartree Fock (HF) and Density Functional Theory (DFT) methods [32-34].

A lot of studies have theoretically investigated different AX₂ types of the structure and TiO₂ structural modifications and their properties. Caravaca et al. [35] have theoretically examined the orthorhombic (Pnma) modification of metal oxides of IV B group of the periodic system of the elements: TiO₂, ZrO₂, and HfO₂, which arise at elevated pressure. At room temperature and the pressure above 30 GPa, the oxides of Zr and Hf pass into the cotunnite type of the structure. The cotunnite structure of titanium dioxide is valid as one of the hardest oxides known to date. The calculations in the mentioned study were performed with the SIESTA code, the DFT method and the generalized gradient approximation - GGA functional with Ceperley-Alder parameterization, while the basis set was described by pseudo-atomic orbitals.

The main properties of the interest were the mechani-

cal properties of these structures, such as hardness and elastic properties the theoretical results of which were compared with experimental ones [35].

The direct band gap values of TiO_2 obtained by different quantum methods and functionals can be found in literature as following: 1.67–3.25 eV (DFT method with local-density approximation - LDA functional), 1.69–4.45 eV (DFT method with GGA functional) and 3.4–13.05 eV (HF method) [36]. Ekuma and Bagayoko [36] have theoretically examined the electronic properties of rutile using DFT and the self-consistent Bagayoko - Zhao - Williams (BZW) method to determine the band gap. The ground state results for rutile were in agreement with the experimental data and suggested a direct band gap value of 3.05 eV. By comparing the experimental and theoretical results, the DFT method and the LDA functional gave a band gap value for rutile about 2 eV, which is 33% lower than the experimentally obtained value (about 3 eV). Using the Perdew - Wang GGA functional (PWGGA), a similar band gap value of 1.93 eV was obtained for rutile, while the result obtained by HF method was higher than the experimental one. Undervaluation of the band gap can be avoided by applying self-interacting corrections, or by using many-body GW approximations. Beck suggested to include part of the HF exchange into DFT energy for the self-interacting corrections. Such a hybrid functional, depending on the percentage of Fock's exchange shows a good theoretical description of the band gap. Zhang et al. [37] used the CRYSTAL code for the calculation of the bulk rutile, anatase, and brookite examined by the DFT method with LDA and GGA functionals with addition of HF exchange. Also, in order to examine the effects of HF exchange functional, a DFT method was used and a hybrid proposed by Moreira et al. [38] which corresponds to the contribution of Dirac-Slater modification, HF exchange and LDA correlation functional, with the delta factor that varied from 0 to 100% (the pure LDA exchange was replaced by pure HF exchange). The values of the results obtained in this way were also compared with the results obtained using PWGGA and B3LYP (Beck for the exchange part and Lee, Yang and Parr for the correlation part of the hybrid functional) hybrids for the same structures. The results showed that the optimal percentage of HF exchange in hybrids was 13% for bulk and surface systems, thereby achieving the highest quality structural parameters and band gap values [38].

One of the latest studies [39] estimated the electronic properties of three different TiO_2 phases, using modified Beck Johnson potential (mBJ) approximation and Boltztrap package, and showed the band gap values of 2.68 eV for rutile, 3.04 eV for anatase and 3.18 eV for brookite. The calculations were performed based on the DFT approximations as implemented in Wien2k code according to the Full Potential-Linearized Augmented Plane Wave (FP-LAPW) [39].

As noted above, rutile is thermodynamically the most stable modification of titanium dioxide modifications but

in practice DFT calculations often give the lower total energy of the system for anatase than for rutile [40]. La-bat et al. [41] applied the HF method and DFT with LDA functional, B3LYP hybrid functional, GGA-PBE (Perdew-Burke-Ernzerhof) functional, and PBE0 hybrid functional to the theoretical testing of anatase and rutile, with LCAO (the linear combination of atomic orbitals method) and PWE (projector-augmented plane wave) basis sets. B3LYP and PBE0 gave results in well agreement with the experimental ones, while the best structural description showed the PBE0 and LCAO basis set. No matter which Hamiltonian was used, the results showed that anatase was more stable than rutile, which is contrary to experimental data [41]. Corrections should be made to the DFT account for long-range van der Waals dispersion interactions or to design a functional that explicitly accounts dispersion in calculation [40]. This is routinely solved by the addition of couple dispersion corrections at the end of the self-consistent DFT account which have proven well for rutile, anatase and some potential titanium dioxide nanostructures; or many-body dispersion which has been done only a few times for metals. Many body dispersion (MBD) methods have been applied by Deringer et al. [40] and the plane-wave DFT method was used for bulk anatase and rutile calculations. Originally, a calculation by DFT method with GGA functional which was corrected by the Tkatchenko-Scheffler (TS) approach was performed, and then the MBD calculation was done for the same modifications. Both types of calculations are based on Hirshfeld's partition scheme for the DFT charge density. The calculation was performed by PAW (projector augment-wave) method implemented in the VASP (Vienna ab initio Simulation Package) software package. The results indicated that the original DFT-GGA calculation gave the wrong, lower energy for the anatase, while the error was reduced by adding dispersion corrections and HF exchange. On the other hand, the DFT-MBD calculation provided an excellent agreement with the experimental data [40]. Similarly, Samat et al. [42] have investigated the phase stability of rutile, anatase and brookite using DFT and DFT+U methods from CASTEP computer code calculations. The results obtained with GGA-PBESol showed that anatase is more stable than rutile and brookite, which disagrees with experimental reports. As a solution, the authors found that the better agreement was achieved with calculations obtained using GGA-PBESol+U [42].

Dong et al. [43] theoretically investigated TiO_2 modification of P42/nmc space group by the CASTEP code and the DFT method. This modification was mechanically stable at pressures above 30 GPa and dynamically stable at 60 GPa. The results show that columbite transits into this structure above 45.8 GPa with the PBE-GGA functional calculation, and above 50.1 GPa with the GGA+U calculations. Also, fluoride type and the P42/nmc structures were assumed to be coexisting, which has been confirmed experimentally [43]. Zhou et al. [44] hypothesized that the fluoride structure experimentally

synthesized is actually obtained as modified form of Pca21. The calculations in that study were performed using the VASP code, and DFT method with PBE-GGA functional. The results showed that the structure Pca21 was stable at temperatures above 476 K and the pressure of 35 GPa, whereas cubic structures of the fluoride and pyrite type were not obtained at any pressure from 0 to 200 GPa.

These results confirm that the experimentally obtained cubic structure should be Pca21 type of titanium dioxide. Also, these calculations showed that rutile was actually a high-temperature phase at ambient pressure. The other theoretical investigations at elevated pressures, such as performed by Muscat et al. [45] showed the transition from anatase to columbite at the pressure of 3.5 GPa, and the transition from rutile to columbite at 21 GPa, using DFT method with different functionals and basis sets as implemented in CRYSTAL code.

Great attention attracted the assumption that baddeleyite, depending on the position of oxygen in a unit cell, may show remarkable hardness of the material. Dewhurst et al. [46] were both interested in baddeleyite and columbite for the theoretical investigation, as well as the fluoride type of TiO₂ (Fm3m) modification that had not been experimentally identified before. Theoretical methods for testing these structures at elevated pressure are usually plane-wave pseudopotential or LCAO modeling. This study concluded that for the production of materials with high hardness is important to use rutile as the initial structure, which at constant increasing of the pressure passes into columbite of similar hardness, while baddeleyite proved to be metastable, with a decrease in the volume and potential returning into rutile. The bulk modulus of fluorite phase was increased by 16% relative to rutile, and the total strength of the material most likely depended on the lengths of Ti–O bonds and the coordination number [46]. Wu et al. [47] have theoretically investigated the TiO₂ phase transitions at elevated pressure: rutile → baddeleyite → OI (orthorhombic I structure) → cotunnite → OII (orthorhombic II structure) and transitions OII → OI → baddeleyite → columbite by pressure decompression. The results showed for all modifications bulk modulus values in the range of 200–240 GPa, while baddeleyite showed the lowest hardness. Cotunnite has not been shown to be superhard as previously experimental works showed [46]. Rutile and columbite have proven to be energetically close structures, with the band gap values for all structures in the range 1.7–2.3 eV [47]. Liu et al. [48] examined the structural, elastic, electrical and optical properties of different titanium dioxide structures.

Ten different TiO₂ modifications were tested: fluoride-type, pyrite, rutile, anatase, hollandite, brookite, columbite, cotunnite, bronze and baddeleyite. The CASTEP code was used for theoretical calculations using pseudopotential and DFT method with LDA, GGA and hybrid B3LYP functionals. The results show that the structural parameters are in good agreement with the available theoretical and experimental results; all 10 modifications

are mechanically stable; the bulk modulus grows with greater density; the shorter Ti–O bonds are, the higher band gap is; the TiO₂ has a covalent character [48].

Shojaee et al. [49] examined the dynamical properties of the rutile and anatase phases of titanium dioxide using a phonon approach to obtain information on thermal and elastic properties. The calculations were performed with the Quantum-Espresso code, a DFT pseudopotential and plane-wave basis set with LDA and GGA functionals. The results showed that the elastic constants obtained by calculations with LDA showed better agreement with the experimental ones. The heat capacity at the room and Debay's temperatures obtained with GGA functional showed better agreement with the experimental data. Sikora [50] calculated the phonon dispersion for rutile, using the VASP code of the ultra-soft pseudopotential of the DFT method with LDA functional. A structure of supercell 2 × 2 × 2 and an equilateral basis set were used. The results showed good agreement with the experimental results obtained by neutron scattering [50].

Guo et al. [51] have theoretically examined the electronic structure and properties of anatase doped with Au, Ag and Cu cations. The calculations have been performed by simulating supercells of 72 atoms for each dopant. Due to the large atomic radius of the oxygen atoms, the titanium atoms were replaced by dopants.

The structural formulas of the supercells were Ti₂₃CuO₄₈, Ti₂₃AgO₄₈, and Ti₂₃AuO₄₈ forming a dopant concentration of 4.17%. The calculations were performed by CASTEP code, the DFT method of the plane-wave pseudopotential, with GGA-PBE functional. The results show that the optical absorption of the doped material is visible in the range 400–1000 nm, while the band gap boundaries shift towards the longwave region compared to pure TiO₂ [51].

In order to enhance the photocatalytic efficiency of TiO₂, one of the potential solutions is shifting its absorption range from UV region into VIS, which can be achieved by metal or nonmetal doping of TiO₂ [51–54]. Wang and Lewis [52] investigated pristine and S doped anatase and rutile structures and their electronic properties. Theoretically determined band gap values for S doped anatase were as follows: 3.26 eV [52], 2.22 [55], 2.0 eV [56] and for S doped rutile: 3.05 eV [52], 2.0 eV [57], 1.78 eV [58], while experimentally determined adopted data found for S doped anatase were 3.2 eV [56], 3.42 eV [57] and for S doped rutile 3.06 eV [58].

The obtained theoretical data of S doping by the same authors [52] suggested that the concentration of doped S lower than 0.26% did not show significant narrowing of the band gap (>3 eV), while the concentration of 5.6% S showed a significant red shift of the valence band edge (2.2 eV for anatase and 2.3 eV for rutile), which means that the photocatalytic properties were improved by doping with the higher concentration of dopants. Those results were in good agreement with experimental data.

The similar study has been performed by Koteski et al. [59] in order to confirm the experimentally determined

enhancement of the visible light absorption of Cu/N co-doped TiO_2 anatase 101 surface. The same study found the contribution of Cu and N dopants to appearance of hybridized states in the DOS (density of states) of the anatase (101) surface [59]. The similar results of DFT calculations showed the redshift of the optical absorption edge in Fe/Si co-doped anatase [59,60], while another DFT study found that W/N co-doped anatase and rutile contribute to narrowing of the band gap [59,61]. Similar studies were performed by other authors, such as In/N co-doping of anatase [62], with creating oxygen vacancies, and N doping of rutile [63], using DFT method and GGA-PBE and GGA+U approximation and functionals, respectively. The reduction of the band gap and shifting of the absorption spectrum towards the visible regime were noticed in both cases [62,63].

Chen et al. [64] have predicted bulk TiO_2 structures with a low band gap values using a global optimization by MODE (multiobjective differential evolution – MODE) method. The DFT method was used for structural relaxation and calculations of electronic structure, with LDA functional, implemented in VASP code. The results showed the band gaps' values of the new structures PI (Pnma) and CI (C2) of 1.95 and 2.64 eV, respectively [64]. Bedghiou et al. [65] performed global minimizations of rutile TiO_2 band gap using first-principles calculations combined with the algorithm USPEX (Universal Structure Prediction: Evolutionary Xtallography) to predict new TiO_2 phases at high/ultrahigh pressure. The results showed that the compression leads to reversible semiconductor-to-metal, metal-to-semimetal and semiconductor-to-semimetal transitions in rutile. All used approximations and functionals GGA, GGA+U, and HSE06 overestimated the band gaps predicted by USPEX. In this study, USPEX has successfully discovered new TiO_2 phases with very low band gaps and new stable TiO_2 polymorph with the lowest direct band gap recorded for titanium dioxide (0.26 eV) [65].

The investigation of the electronic properties of mobile oxygen vacancies in TiO_2 , which have been recognized as the source for resistive switching (RS) behavior, is of great importance for developments in information technology and potential application in new types of memory devices [30]. Nadimi et al. [30] have employed DFT and DFT+U to calculate the electronic structure of oxygen vacancies in anatase TiO_2 crystal and suggested $U = 3.5$ eV value for the Hubbard term (U) for the calculations of the migration of oxygen vacancies. The authors have found that the energetically most favorable charged state for oxygen vacancies within the anatase is the $q = +2$ state [30].

Another AX_2 type of compound, MoS_2 , has attracted great attention because of the value of its direct band gap (1.90 eV) [31]. Li et al. [31] proposed novel design schemes based on the 2D $\text{MoS}_2/\text{TiO}_2$ heterostructure and superlattice and have investigate its electronic properties for the application as a solar cell and photocatalyst. The study was performed by DFT method with the

generalized gradient approximation (GGA) for the PBE exchange-correlation functional, implemented in the VASP code. This heterostructure could have potential applications in many fields such as photoelectric devices, photocatalysis, energy conversion and storage, as well as biomedicine, etc [31].

Conclusion

Titanium dioxide, TiO_2 , as an oxide of the AX_2 -type of structure has been presented in this work following its electronic structure and properties of various modifications, potential application and an overview of the scientific literature. An overview was based on the most characteristic features of this material examined by theoretical approach, as well as the current problems that can be encountered in calculations and compared with experimentally obtained data.

Based on the scientific reports, it can be concluded that TiO_2 crystal has a covalent character and that the structure cause its properties such as the value of bulk modulus that grows with greater density, the shorter Ti–O bonds are the higher the band gap is, while the hardness of TiO_2 modifications depends on the arrangement of oxygen atoms in the unit cell. Regarding the TiO_2 crystal modifications, rutile is a high-temperature phase at the ambient pressure; fluoride and pyrite types of the structure are difficult to obtain experimentally and theoretically, so they actually appear modified as orthorhombic Pca21 structures instead of a cubic form. The other types of AX_2 compounds, such as the oxides of Zr and Hf, pass into a cotunnite structure at the room temperature and the pressure above 30 GPa. It is recommended to start synthesis of superhard TiO_2 materials from the rutile structure. The local functionals in theoretical calculations does not describe well the band gap in TiO_2 electronic structure, so the corrections, such as hybrid functionals, need to be added. Disagreement of theoretically and experimentally obtained results of the anatase and rutile ground state can be overrun by adding dispersion correction explicitly into the account, by adding pairwise dispersion corrections at the end of the DFT account, or with a many-body approach for long-range interactions, while some authors performed GGA-PBESol+U instead of GGA-PBESol, and other hybrid functionals. Hartree Fock's exchange of 13% added in the DFT method calculations proved to be the optimal correction for accounts with hybrid functionals. The band gap values of TiO_2 obtained theoretically by the HF method are higher than the ones obtained experimentally, while the calculations with approximative functionals underestimate band gap values. The improvement of the photocatalytic efficiency of TiO_2 can be achieved by metal or nonmetal doping, while designing of heterostructures and creating mobile oxygen vacancies could be of the great importance for developments in information technology and producing of solar cells. Nowadays, different methods for structure prediction can contribute to the investigation of new AX_2

phases and structures and their properties.

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Izvod

AX₂-TIP JEDINJENJA I PREGLED TEORIJSKOG ISPITIVANJA TiO₂Dušica Jovanović ^{1,2}, Jelena Zagorac ^{2,3}, Branko Matović ^{2,3}, Aleksandra Zarubica ¹,(PREGLEDNI RAD)
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DOI: 10.5937/savteh2002079J¹Prirodno-matematički fakultet u Nišu, Univerzitet u Nišu, Niš, Srbija²Institut za nuklearne nauke Vinca, Laboratorija za nauku o materijalima, Univerzitet u Beogradu, Beograd, Srbija³Centar za sintezu, procesiranje i karakterizaciju materijala za primenu u ekstremnim uslovima -CextremeLab, Beograd, Srbija

Jedinjenja opšte formule AX₂ mogu biti jonskog, kovalentnog ili molekulskog tipa strukture, što zavisi od veličine atoma koji ih izgrađuju i njihovih polarizacionih osobina. Materijali ovog tipa strukture poseduju osobine koje nalaze primenu u različitim oblastima nauke i industrije. Titanijum dioksid, kao jedinjenje opšte formule AX₂ i materijal sa poluprovodničkim osobinama širokog opsega vrednosti direktnog band gap-a, često je istraživao zbog svojih fotokatalitičkih osobina i različitih primena poput proizvodnje solarnih ćelija, odstranjivanja različitih zagađivača, eliminacije mikroorganizama, zaustavljanja rasta ćelija određenih vrsta kancera, itd... Eksperimentalne i teorijske studije čiji je predmet istraživanja ovaj metalni oksid, pružaju različite podatke o stabilnosti njegovih kristalnih modifikacija i o njihovim faznim prelazima. U ovom radu je predstavljen pregled teorijski ispitivanih modifikacija TiO₂ i aktuelnih problema na koje se može naići prilikom izvođenja računa (poput dobijenih različitih vrednosti band gap-a u zavisnosti od primenjene metode i funkcionala; razlika u stabilnosti modifikacija ispitivanih na ab initio nivou i eksperimentalno; karakter hemijskih veza i prelazi na određenim temperaturama i pritiscima...), kao i prevazići dodatkom određenih korekcija u postavci računa.

Ključne reči: jedinjenja opšte formule AX₂, TiO₂, ab initio, teorijski računi