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The Effect of High Pressure on the Energy Gap in Photocatalytic Semiconductors

S. A. Mawlood

Department of Physics, College of Science, Salahaddin University-Erbil, Erbil, Iraq

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Correspondence:
Salar Ali Mawlood
Salar.mawlood@su.edu.krd

Abstract

In this study, we examine the high-pressure energy bandgap of several photocatalyst semiconductors (ZnO, MgO, CdO, WO_3, CaO, SnO_2, In_2O_3, ZrO_2, ZnS, and TiO_2) by applying the Angilella equation. This equation helps analyze the change in energy gap with pressure, relative to the variation in lattice constant. The Murnaghan equation of state (EOS) was used to calculate the pressure. The validity of the Angillela equation is confirmed only for cubic ZnO, wurtzite MgO, and rock salt CdO, but for other semiconductors(WO_3, CaO, SnO_2, In_2O_3, ZrO_2, ZnS, and TiO_2), it is found that the Angillela equation is not valid precisely. Our results indicate that the energy gap of these photocatalyst semiconductors behaves similarly to that of other semiconductors under high pressure, with an increase in energy gap as pressure rises. Additionally, our results reveal that the lattice constant decreases as pressure is applied for all photacatalyst semiconductors used in this work.

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1. Introduction

Photocatalysis, particularly semiconductor-based photocatalysis, has garnered significant attention due to the unique properties of semiconductors that make them ideal for most photocatalytic processes. One of the fundamental aspects of photocatalysis is the bandgap, as its analysis helps determine the catalytic potential of a material. Photocatalysis has emerged as a topic of great interest, especially for its wide-ranging applications in environmental decontamination, where it can degrade a variety of compounds **[1]**. High-pressure research has evolved into an interdisciplinary field with important applications across various scientific domains. It provides an effective driving force for the formation of new material structures, thereby enabling the discovery of novel material properties. Studying the effects of high pressure is essential not only for understanding the materials in our environment but also for creating entirely new forms of matter. Over the last three decades, semiconductor photocatalysis has been extensively studied as a promising approach for addressing both energy generation and environmental challenges. Research has shown that the energy gap in CsNbO3 photocatalysis is pressure-dependent, with insights derived from first-principles calculations **[2]**. Similarly, the limitations of equations of state (EOS) have been explored for AlN and CuO photocatalyst semiconductors under high pressure **[3]**. Pressure has also been used to engineer the bandgap and photoelectric response of C_3N_4 **[4]**. In this study, we investigate the pressure-dependent bandgap behavior of various photocatalyst semiconductors using the equation proposed by Angilella *et al.,***[5]**. To determine the pressure, we employ the Birch-Murnaghan equation of state **[6]** and assess the validity of Angilella's equation for modelling the pressure dependence of band gaps in these materials.

2. Theoretical Analysis:

The energy band gap E_g of materials as a function of the lattice constant can be calculated using the equation provided by Angilella *et al.* **[5]**:

$$E_g = A\left(1 - \sqrt{\frac{a_p}{a_c}}\right)^{\gamma} \qquad \ldots\ldots (1)$$

Here a_p is the lattice constant under pressure, while the fitting parameters are a_c=6.7797 A^o , A=50.21 eV, and γ=1.71675, which are general parameters for all kinds of semiconductors. The lattice parameter dependence on pressure can be determined using the Murnaghan equation of state **[7]**:

$$a_p = a_o\left(1+\frac{B'}{B}p\right)^{\frac{-1}{3B'}} \qquad \ldots\ldots\ldots (2)$$

Here B, B' are the bulk modulus and its first pressure derivative at $p=0$, a_o is the lattice constant at ambient conditions of the material, and p is the pressure. By combining equations (1) and (2), the energy gap at high pressure can be expressed as :

$$E_g = A\left(1-\sqrt{\frac{a_o\left(1+\frac{B'}{B}p\right)^{\frac{-1}{3B'}}}{a_c}}\right)^{\gamma} \qquad \ldots..(3)$$

To evaluate the effect of high pressure on the energy band gap, Birch-Murnaghan EOS **[6]** is used:

$$P = \left(\frac{3B}{2}\left(\eta^{-7/3}-\eta^{-5/3}\right)\left[1+\frac{3}{4}(B'-4)\left(\eta^{-2/3}-1\right)\right]\right) \qquad \ldots.(4)$$

where $\eta = \frac{V_p}{V}$, V_p is the volume of material under pressure, and V is the volume of material at p=0. So the energy band gap under high pressure can be written as:

$$E_g = A\left(1-\sqrt{\frac{a_o\left(1+\frac{B'}{B}\left(\frac{3B}{2}\left(\eta^{-7/3}-\eta^{-5/3}\right)\left[1+\frac{3}{4}(B'-4)\left(\eta^{-2/3}-1\right)\right]\right)\right)^{\frac{-1}{3B'}}}{a_c}}\right)^{\gamma} \qquad \ldots.(5)$$

3. Results and Discussion:

In this study, we analyzed the energy band gap of photocatalyst semiconductors by calculating the energy gap under varying high-pressure conditions using the equation proposed by Angilella *et al.* **[5]**. The variation of the energy band gap with increasing pressure is calculated by equation (5) for various photocatalyst semiconductors.

Input values of lattice constants (a_o), Bulk modulus (B) and its first pressure derivative (B'), also energy gap at ambient pressure (E_g) for photocatalyst semiconductors are shown in Table 1. The graph depicting the relationship between the energy band gap (E_g) with high pressure (P) using equation (5) for ZnO, MgO and CdO semiconductors are shown in figures (1-3).

Table (1). Parameters values for photocatalyst semiconductors: lattice constant (a_o), Bulk modulus (B) and its first pressure derivative (B'), and energy gap at ambient pressure (E_g)

Material	**lattice constant (A^o)**	***B* (Gpa)**	***B′***	**E_g(eV)**
rocksalt ZnO	4.33 [8]	228 [8]	4 [8]	3.2[8]
wurtzite MgO	3.32 [8]	132 [9]	4.34 [9]	6.4[9]
rocksalt CdO	4.65 [10]	128 [10]	5.08 [10]	2.28[10]
cubic WO_3	3.75 [11]	205 [11]	3.541 [12]	2.62[11]
cubic CaO	4.8105 [13]	111 [13]	4.1 [13]	4.58[13]
rutile SnO_2	4.699 [14]	244.7 [14]	4.44 [14]	3.68[15]
cubic In_2O_3	5.485 [16]	187.87[16]	4 [16]	3.7 [17]
tetragonal ZrO_2	3.591[18]	170 [18]	4.3 [18]	4.1[19]
zinc-blend ZnS	5.41 [20]	77 [20]	4 [20]	3.73[21]
rutile TiO_2	4.586 [22]	211 [22]	6.5 [22]	3[22]

From figures (1), (2), and (3), reducing the lattice constant of the semiconductor clearly increases pressure across all three materials, ZnO, MgO and CdO, respectively. Furthermore, for ZnO, MgO and CdO photocatalyst semiconductors at high pressure, our results indicate that the energy bandgap increases with increasing pressure.

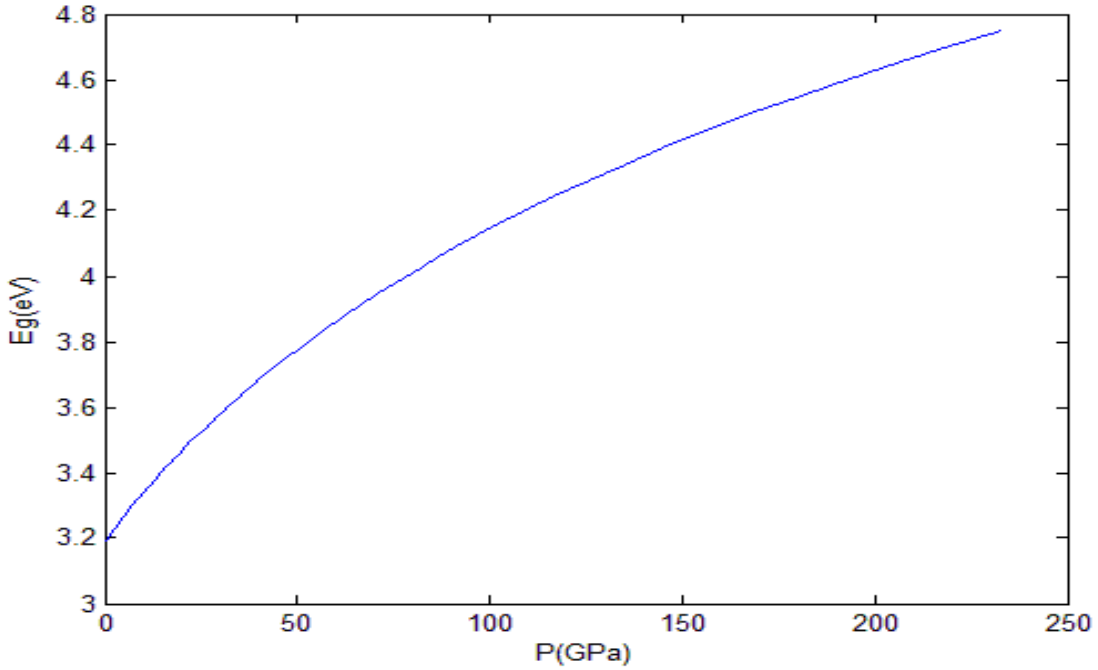

Figure 1. pressure dependence of energy gap of rocksalt ZnO

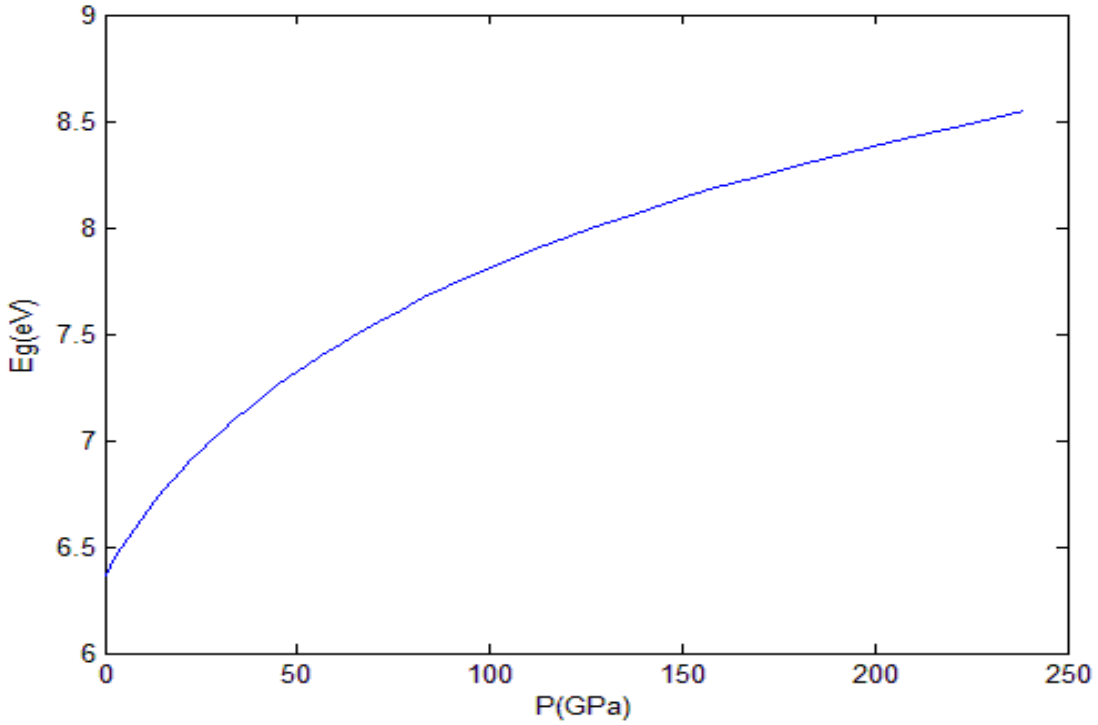

Figure 2. pressure dependence of energy gap of wurtzite MgO

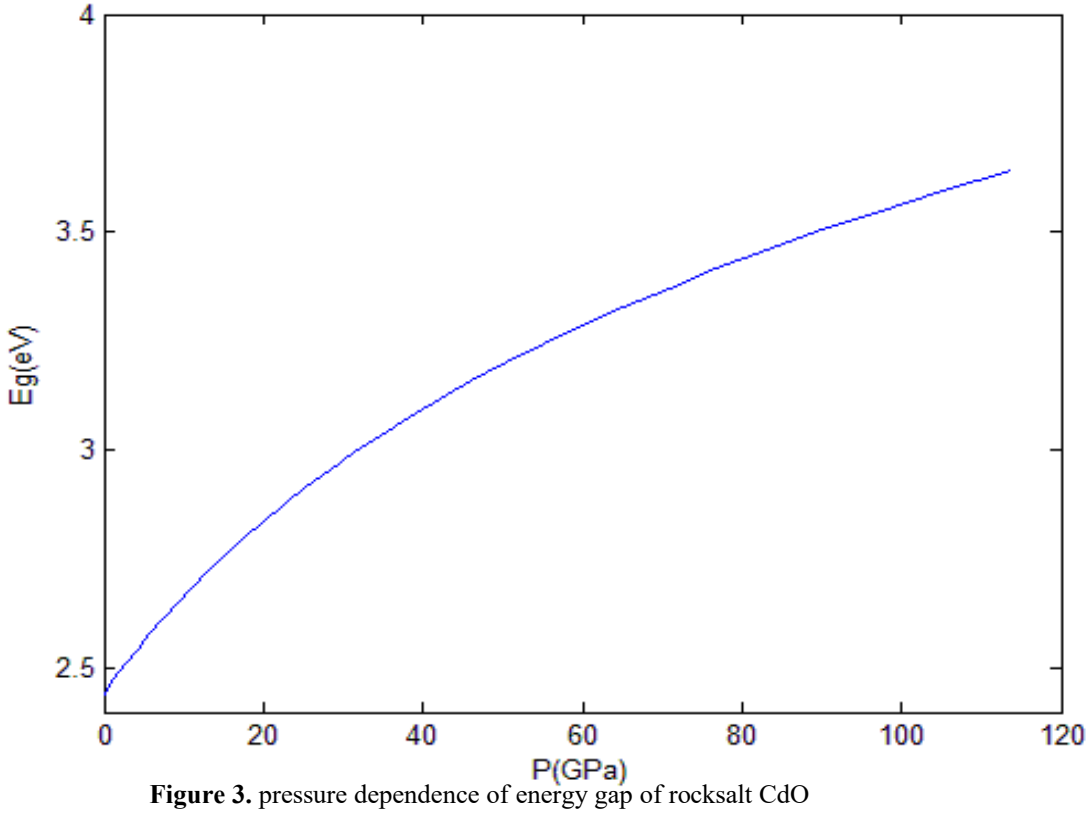

Figure 3. pressure dependence of energy gap of rocksalt CdO

The energy bandgap of photocatalyst semiconductors similarly behaves like other semiconductors when affected by high pressure. For those three materials above, we take the value of pressure to the limit of the phase transition value of those materials, because for pressure above that limit, the material changes its phase to another phase, resulting in a change from direct bandgap to indirect bandgap due to high pressure.

In figures (1), (2) and (3) we also observe that Angelilla equation **[5]** is valid for ZnO, MgO and CdO respectively respect to energy gap, where for ZnO, we have energy gap E_g= 3.2 eV **[8]** also its clear from fig. 1, where for pressure P=0, E_g=3.2 eV also, so we can say that Angilellla equation is valid for ZnO energy gap variation with pressure, the same thing it true for MgO, where its energy gap E_g=6.4 eV **[9]** and that's clear from fig. 2, that this value obtained when pressure is zero, and for CdO photocatalyst semiconductor, its energy gap E_g= 2.28 eV **[10]**, and obtained from fig. 3 , Eg=2.4 eV, so the Angilella equation is valid for those three materials for the variation of energy bandgap with pressure, because from figures (1), (2) and (3), the value of energy gap for these materials when p=0 is identical to the values of ambient energy gap for these materials from table (1)

A graph plotted showing the relationship between the energy bandgap and pressure for photacatalyst semiconductors (WO3, CaO, SnO2, In2O3, ZrO_2, ZnS and TiO2) are shown in Figures (4) to (10).

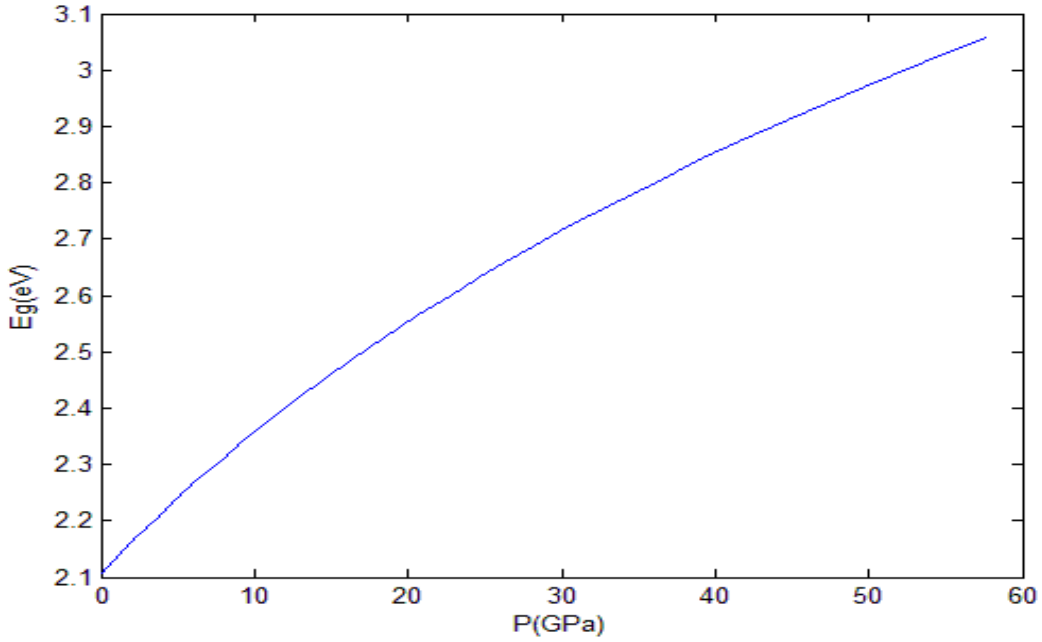

Figure 4. pressure dependence of energy gap of cubic WO_3

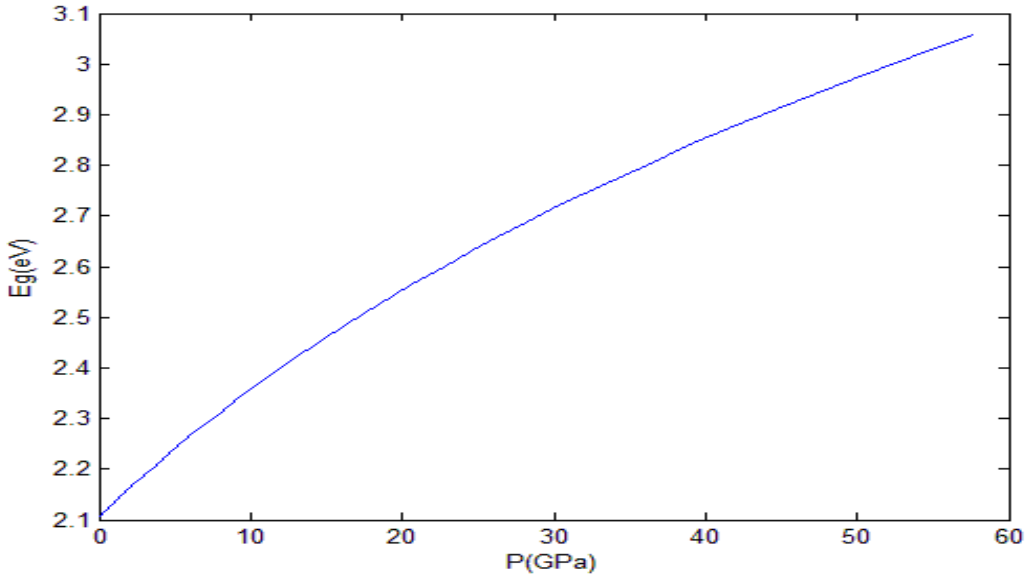

Figure 5. pressure dependence of energy gap of cubic CaO

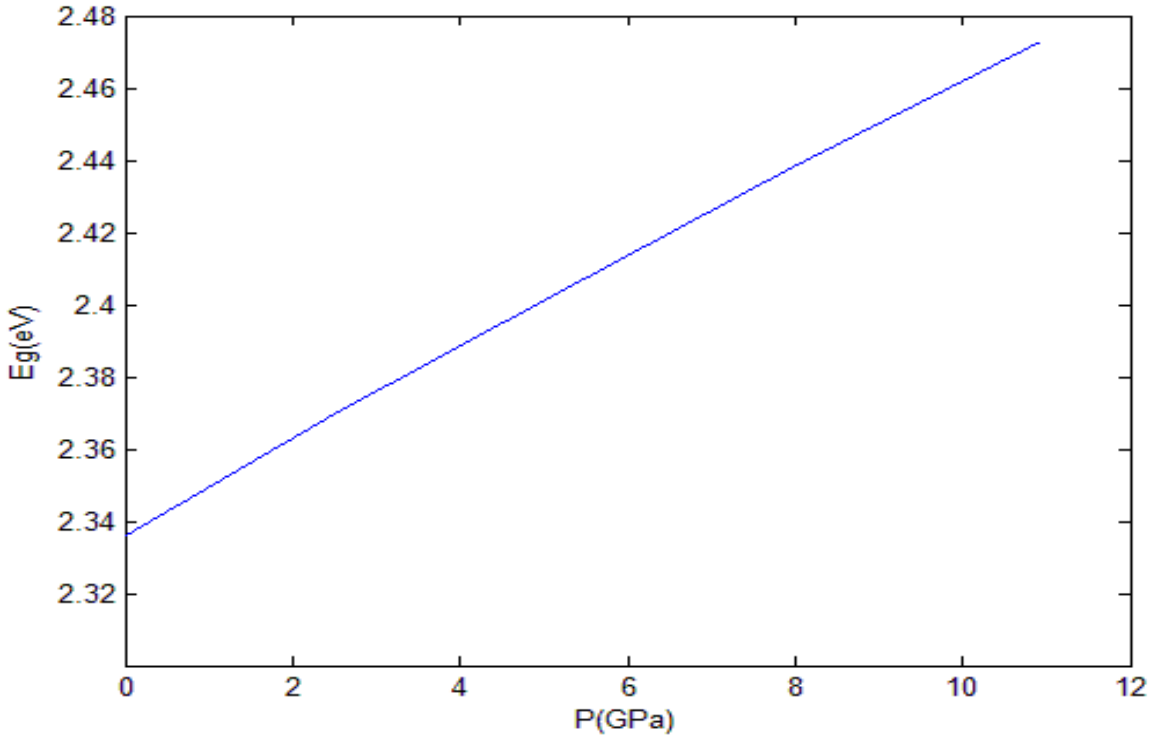

Figure 6. pressure dependence of energy gap of rutile SnO_2

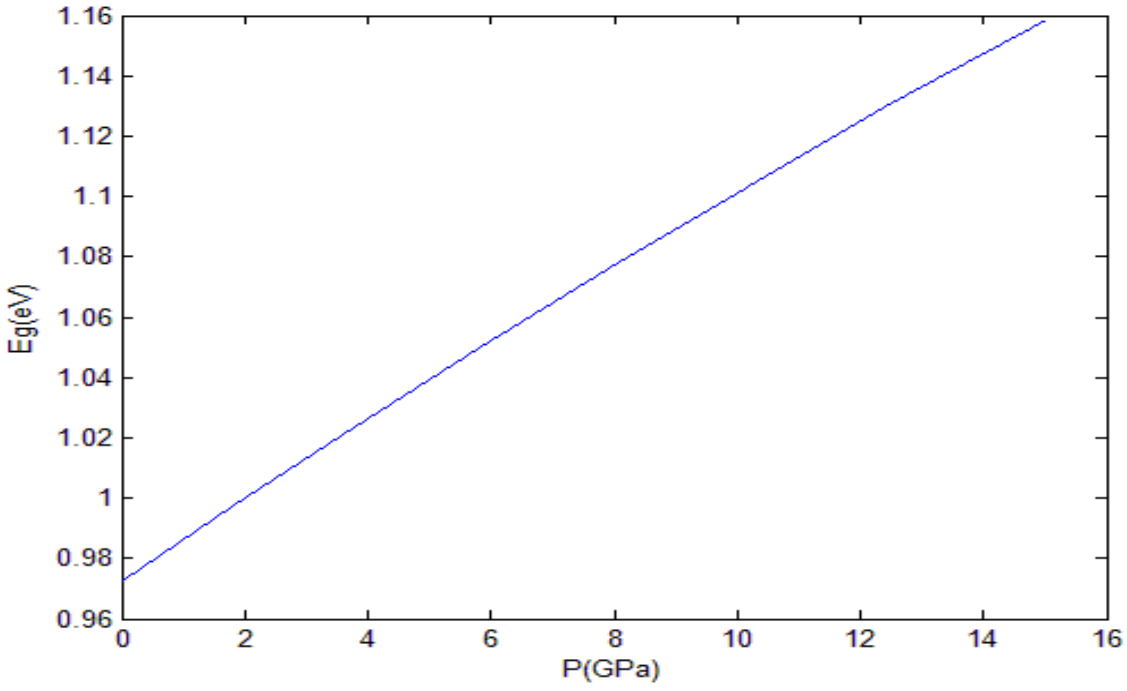

Figure 7. pressure dependence of energy gap of cubic In_2O_3

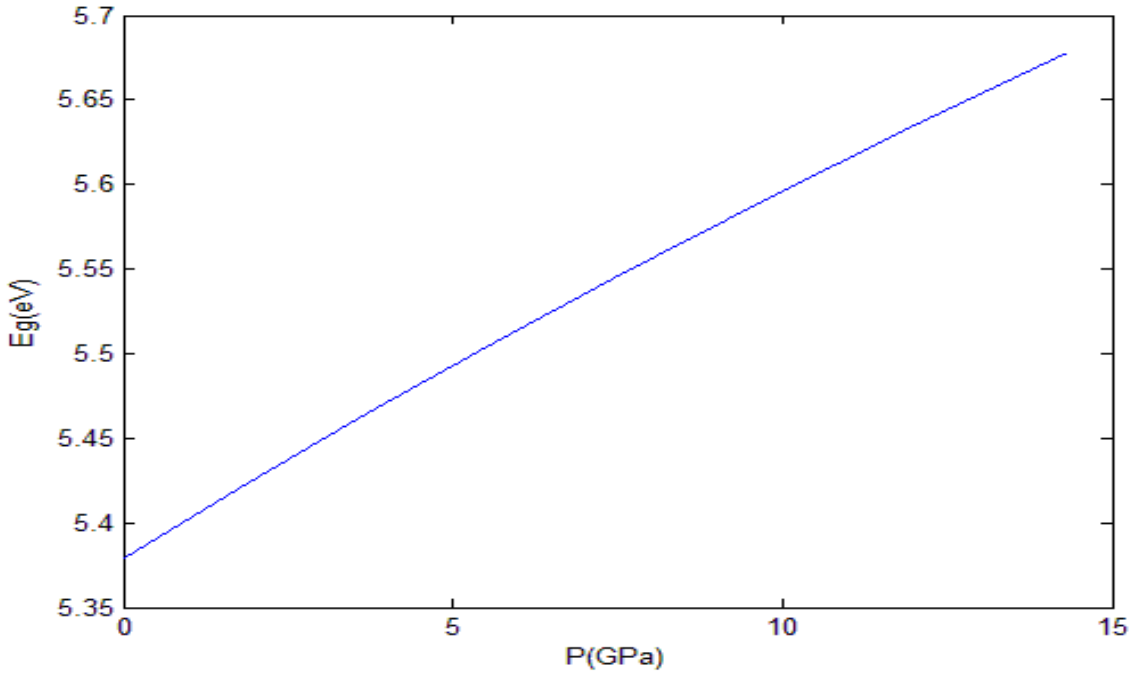

Figure 8. pressure dependence of energy gap of tetragonal Zr_2O_3

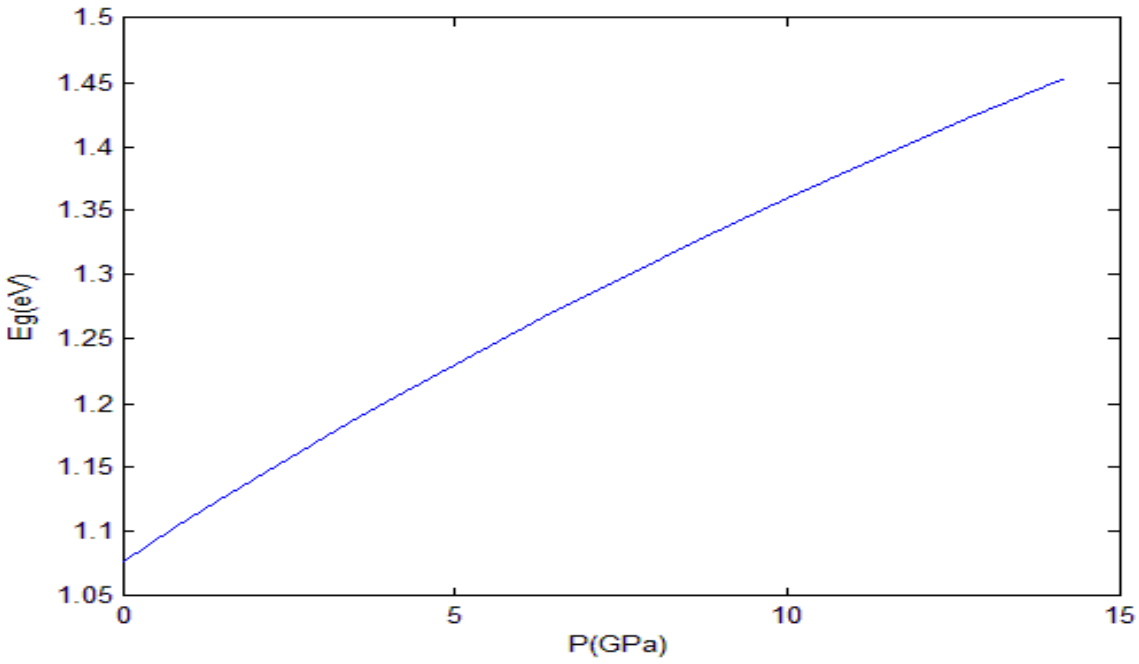

Figure 9. Pressure dependence of energy gap of Zinc-blende ZnS

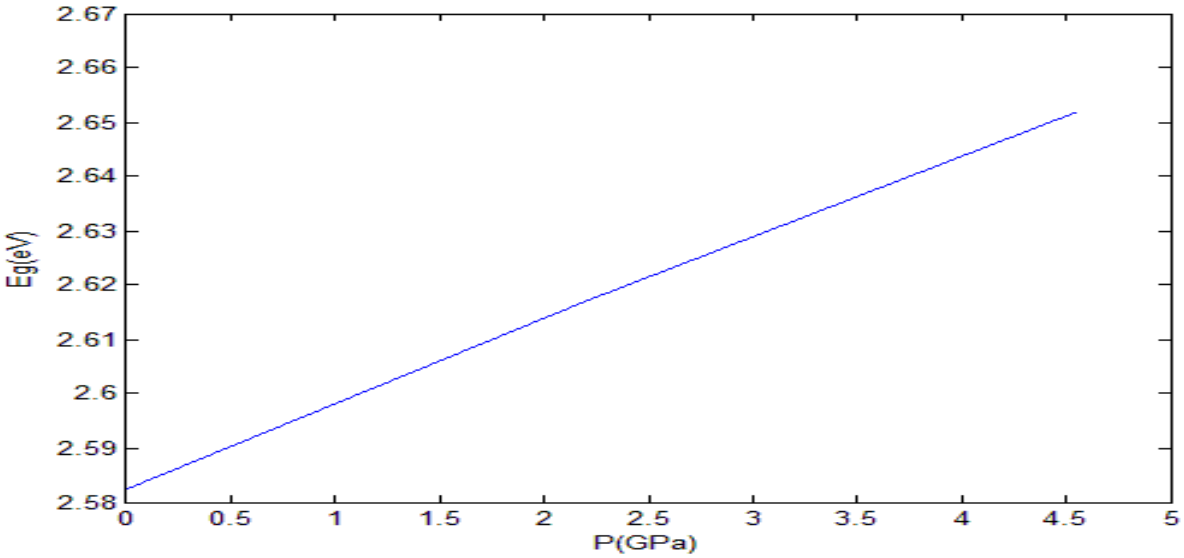

Figure 10. pressure dependence of energy gap of rutile TiO_2

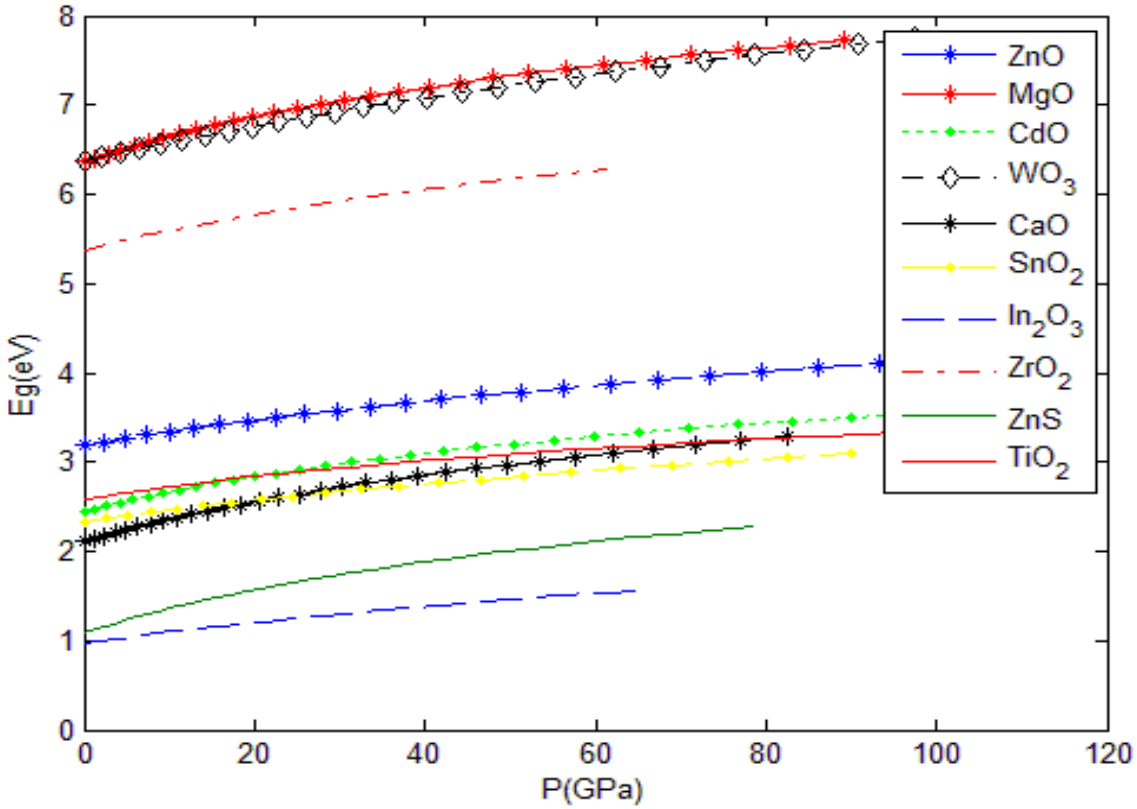

Figure 11. pressure dependence of energy gap for all photocatalytic semiconductors used in this workrutile TiO_2

From figure (4) to figure(10), it shows that increasing the pressure leads to a corresponding increase in the energy gap for all photocatalyst semiconductors. (WO_3, CaO, SnO_2, In_2O_3, ZrO_2, ZnS and TiO_2), but we observe that when the ambient energy bandgap of the photacatalyst semiconductor from Table 1 is not identical with the energy bandgap for photocatalyst semiconductor when P=0 from the figures (4-10), so for those materials Angelilla's equation is not valid.
Figure (11). Show the pressure dependence on energy bandgap for all photocatalytic semiconductors used in this work, it's clear that for all materials, as high pressure increases energy bandgap also.

Table(2). Energy bandgap values at ambient pressure and Energy bandgap calculated from Figure (11) at p=0 for all photocatalytic semiconductors used in this work

Material	Energy gap at ambient pressure	Energy gap from fig. 11 when p=0
ZnO	3.2	3.2
MgO	6.4	6.37
CdO	2.28	2.4
WO_3	2.62	4.85
CaO	4.58	2.1
SnO_2	3.68	2.336
In_2O_3	3.7	0.973
ZrO_2	3.591	5.34
ZnS	3.73	1.08
TiO_2	4.586	2.586

Its clear from Table 2 that Energy gap at ambient pressure is close to energy gap from Fugure. 11 when p=0 for (ZnO, MgO and CdO), and the values of energy gaps for other materials (WO_3, CaO, SnO_2, In_2O_3, ZrO_2, ZnS and TiO_2) are not matches, therefore the Angillela equation is accurately valid for (ZnO, MgO and CdO), but not valid correctly for other materials.

4. Conclusion

The analysis concludes that the Angilella's equation, which describes the variation of the energy bandgap with pressure using the Murnaghan EOS, is valid exclusively for ZnO, MgO, and CdO photocatalyst semiconductors. This equation, however, does not accurately describe the behavior of the other photocatalyst semiconductors (WO_3, CaO, SnO_2, In_2O_3, ZrO_2, ZnS and TiO_2). The pressure values considered are constrained to the phase transition limits of the respective materials. The results indicate that a decrease in the lattice constant leads to an increase in pressure. Moreover, under elevated pressure conditions, the energy bandgap exhibits an increasing trend with pressure according to the Birch-Murnaghan EOS, indicating that the pressure dependence of the bandgap in photacatalyst semiconductors parallels that observed in conventional semiconductors subjected to high-pressure environments.

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7. Ethical approval: The author declares that he is the sole contributor to this manuscript. This manuscript is the author's own original work and has not been published elsewhere.

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تأثير الضغط العالي على طاقة الفجوة في أشباه الموصلات الضوئية

سالار علي مولود

قسم الفيزياء، كلية العلوم، جامعة صلاح الدين-أربيل، اربيل، العراق

المستخلص

في هذه الدراسة، تم تحليل تأثير الضغط العالي على فجوة طاقة النطاق لعدة اشباه الموصلات الضوئية (ZnS, ZrO_2 , ,ZnO, MgO, CdO, WO_3, CaO, SnO_2 , InO_2 و TiO_2) من خلال تطبيق المعادلة التي قدمها Angillela. تساعد هذه المعادلة في تحليل التغير في فجوة الطاقة مع الضغط نسبة الى التغير في ثابت الشبيكة البلورية. لحساب الضغط استخدمنا معادلة الحالة لـ Murnaghan . معادلة Angillela أثبتت دقتها مع ZnO المكعب و MgO الهيكلي من نوع ووزرزايت، و CdO من نوع ملح الصخور، فيما كان تطبيق المعادلة لبقية أشباه الموصلات ليست دقيقة تماماً. تظهر نتائجنا أن فجوة الطاقة لهذه أشباه الموصلات الضوئية تتصرف بشكل مشابه لأشباه الموصلات الاخرى تحت الضغط العالي، حيث تزداد فجوة الطاقة مع زيادة الضغط بالإضافة إلى ذلك، بينت النتائج ان ثابت الشبيكة يقل مع تطبيق الضغط لجميع أشباه الموصلات الضوئية المستخدمة في هذا العمل