First Principle Calculations for Silver Halides AgBr, AgCl, and AgF

Akram H. Taha

Department of Physics, Faculty of Science and Health, Koya University, Koya KOY45, Kurdistan Region - F.R. Iraq

Abstract—**Density functional theory (DFT) coupled with Generalized Gradient Approximation (GGA) method are carried out to calculate the electronic structures of AgX (X; Br, Cl, and F). The effect of hybridizing between 4d orbital of Ag element and the p orbitals of the X in the valence band plays a very important role in the total density of states configuration. The electronic structure has been studied and all results were compared with the experimental and theoretical values. The importance of this work is that there are insufficient studies of silver halides corresponding the great importance of these compounds. Almost all the results were consistent with the previous studies mentioned here. We found the band gap of AgX to be 2.343 eV, 2.553 eV, and 1.677 eV for AgBr, AgCl, and AgF, respectively, which are in good agreement with the experimental results.**

Index Terms—**Density functional theory; Generalized gradient approximation; Silver halides; Density of states**

1. Introduction

Density functional theory (DFT) is one of the most important theories that can be used to simulate the chemical and some of the physical properties. Many codes with some specific methods of approximations has been used this theory (such as Gaussian 09, WIEN2K, Quanta, SUESTA, …etc) because of its flexibility in writing codes and programming. Some of these codes are free and others are commercial. ab-initio calculations success is due to the fact that they don't require a lot of inputs rather than they are parameter free. In addition, the improvements in algorithms and computer facilities which can be more applicable with the increasing physical and chemical phenomena (Jonathan et al., 2019).

One of the most important compounds used in photographic process are silver halides (James, 1977). Photo- catalytically, silver chloride layer AgCl plays a key role in the oxidation of water to O_2 (Lanz, Schürch and Calzaferri, 1999; Calzaferri et al., 2001). Due to Silver halide's excellent photocatalysts performance, it received huge attention from researchers (Changhua et al., 2016). (Masahiro et al., 2021) developed an *in situ* diffracted X-ray flash to observe high-resolution diffraction patterns from the single crystal grains with a time resolution of 50 ms. The diffraction spots of single grains of silver and silver halides moved in two directions during the photochemical reaction. The motions of the spots represent tilting and rotational motions.

The augmented plane wave (APW) method was used to calculate both valance and conduction bands of silver bromide and silver chloride. For both crystals, the calculated bands were adjusted so that the experimental value of the direct band gap at Γ was duplicated (E_g=5.13 eV in AgCl, E_g=4.29 eV in AgBr). The calculated indirect band gaps were 3.28 and 2.89 eV for AgCl and 2.67 eV for AgBr, respectively (Peter 1965). Self-consistent local density calculations of the electronic structures of AgF, AgCl and AgBr are carried out by the tight binding linearized muffin-tin orbital-atomic sphere approximation (TB LMTO-ASA) method (Onwuagba, 1996). The silver halides rock salt structure has competing minimum in the conduction band at X and Γ points (Gordienko, Zhuravlev and Poplavnoi, 1991). The full-potential linear augmented-Slater-type-orbital implementation of the local-density approximation is employed to stimulate the electronic structure of five of silver halides. The calculated band gaps and bandwidths were in good agreement with the experimental results (Victora, 1997). Silver bromide, silver chloride, and silver fluoride have been subjected of many different quantum investigations. The electronic properties described in the early calculation work done by Scop (Scop, 1965; Bassani, Knox and Fowler, 1965).

The present work depends on the first principle, *i.e.*, the only inputs are the positions of the nuclei. SIESTA code (Spanish Initiative for Electronic Simulations with Thousands of Atoms) under LINUX can provide total energies, stress, and forces using the atomic orbitals with finite-support basis orbitals are the key for calculating the Hamiltonian and overlap matrices in O (N) operation. The used basis set in running the code play key role for more accurate calculations. The electron-ion interaction is represented using pseudopotentials which all plane wave codes do. The used basis set was the double zeta basis plus polarization (DZP) to give minimal angular momentum *l*. where zeta is given in the following wave function (Milton and Stegun, 1964):

$$\Psi_{nlm}(\boldsymbol{r}) = r^{n-1}e^{-\xi r}Y_{lm}(\theta,\phi) \qquad (1)$$

The DFT coupled with generalized gradient approximation (GGA) (Perdew, Burke and Ernzerhof, 1996) is used in this

work to simulate the electronic structure for silver halides using SIESTA free code.

II. Theory

As we mentioned that the DFT is one of the promising theories that can be used to predict behavior of the atoms and molecular moreover, so a brief theory will be discussed here. This theory is concerned with ground state of the system and the basic variables that deals with is the density of the electron $\rho(\vec{r})$ instead of the wave function $\psi(r_1, r_2, \ldots, r_N)$.

For an insulated N-electron system in the Schrödinger equation is:

$$\hat{H}\psi(r_1, r_2, \cdots, r_N) = E\psi(r_1, r_2, \cdots, r_N)$$

(2)

Where the Hamiltonian is

$$\hat{H} = -\underbrace{\sum_i \frac{\hbar^2}{2m_e}\nabla^2_{\mathbf{r}_i}}_{(K.E)_e} - \underbrace{\sum_i \frac{\hbar^2}{2M_i}\nabla^2_{\mathbf{R}_i}}_{(K.E)_n} + \underbrace{\frac{1}{2}\sum_{i \neq j}\frac{1}{4\pi\varepsilon_0}\frac{e^2}{|\mathbf{r}_j - \mathbf{r}_i|}}_{V_{e-e}}$$

$$-\underbrace{\sum_i\sum_j\frac{1}{4\pi\varepsilon_0}\frac{e^2 Z_j}{|\mathbf{R}_j - \mathbf{r}_i|}}_{V_{e-n}} + \underbrace{\frac{1}{2}\sum_{i \neq j}\frac{1}{4\pi\varepsilon_0}\frac{e^2 Z_i Z_j}{|\mathbf{R}_j - \mathbf{R}_i|}}_{V_{n-n}}$$

(3)

Born-Oppenheimer makes use of the large difference between the heavy nucleus mass and the mass of electron ($M_i \gg m_e$), so the Schrödinger equation (3) can be written in the form (Harrison, 2011):

$$\hat{H}_{elec} = -\sum_i \frac{\hbar^2}{2m_e}\nabla^2_{\mathbf{r}_i} + \frac{1}{2}\sum_{i \neq j}\frac{1}{4\pi\varepsilon_0}\frac{e^2}{|\mathbf{r}_j - \mathbf{r}_i|}$$

$$-\sum_i\sum_j\frac{1}{4\pi\varepsilon_0}\frac{e^2 Z_j}{|R_j - \mathbf{r}_i|}$$

(4)

After solving this equation one can get the electronic wave functions (eq. 1) and the energies of the electrons as a function as position. By using the DFT, the dependency can be changed from the coordinates of the electrons to the electron density $\rho(\mathbf{r})$. This theory deal with total electron density instead of many-body Schrödinger wave functions and all calculations were done assuming the ground state of the system. For an N-particle system by integrating the N-particle distribution probability density function $\rho(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_N)$ over $N-1$ variables, as (Carlos, Nogueira and Marques, 2003)

$$\rho(\mathbf{r}_1) = N\int \cdots \int P(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N)\ d^3r_2\, d^3r_3 \cdots\cdots d^3r_N$$

(5)

The Basis set that is used in DFT is the Kohn-Sham (KS) theorem, which is represented by (Hohenberg and Kohn, 1964; Kohn and Sham, 1965):

$$E_{V_{ext}}[\rho(r)] = \underbrace{T_e[\rho(r)] + V_{e-e}[\rho(r)]}_{F_{HK}[\rho(r)]} + \underbrace{V_{e-n}[\rho(r)]}_{V_{ext}[\rho(r)]}$$

$$= F_{HK}[\rho(\mathbf{r})] + \int \rho(\mathbf{r})\, V_{ext}(\mathbf{r})\, d^3r$$

(6)

This equation represents the first KS theorem which states that "For any system of interacting particles in an external potential V_{ext}, the external potential V_{ext} is uniquely determined, apart from an additive constant, by knowledge of the ground-state electron density $\rho_o(r)$."

Where $T[\rho(r)]$ is the kinetic energy, the potential energy is $V_{ext}[\rho(\mathbf{r})]$ and $F_{HK}[\rho(\mathbf{r})]$ is the *Hohenberg-Kohn* universal constant and all are *functionals* of the density $\rho(\mathbf{r})$.

The second KS theorem "*For a trial electron density $\rho_t(\mathbf{r})$, with properties $\rho_t(\mathbf{r}) \geq 0$ and $\int\rho_t(\mathbf{r})\, d^3r = N$ (number of electrons), will give an energy higher than ⟨or equal to, if it were exactly the true electron density $\rho_o(\mathbf{r})$⟩the true ground-state energy $E_{V_{ext}}[\rho_o(r)]$* ," $\left(i.e.\ E_{V_{ext}}[\rho_t(r)] \geq E_{V_{ext}}[\rho_o(r)]\right)$

The GGA exchange-correlation energy can be written as follows (Becke, 1988):

$$\begin{bmatrix} E_{xc}^{GGA}\ [\rho_\uparrow(r), \rho_\downarrow(r)] = \int \rho(\mathbf{r}) \in_{xc}^{GGA} \\ [\rho_\uparrow(r), \rho_\downarrow(r), \nabla\rho_\uparrow, \nabla\rho_\downarrow]\, d^3r \end{bmatrix}$$

(7)

III. Results and discussion

The band structure of the three silver halides is shown in Fig. 1. The kgrid is chosen to be 15 Angstroms. The kgrid is chosen to be 15 Angstroms, which represents the kgrid cutoff that determines the fineness of the k-grid used for Brillion zone sampling. We can estimate the differences in the gap energies some times by expecting a smaller band gap when decreasing the unit cell constant

We can estimate the differences in the gap energies some times by expecting a smaller band gap when decreasing the unit cell constant. A stronger interaction between atom to atom distance and hence a stronger splitting the smaller sizes of these halides, the radii of ions, can compensate this effect. To make the comparison we can use the equation (Glaus and Calzaferri, 2003):

$$\Delta_E = 2\{r(X^-) + r(Ag^+)\}/a(AgX)$$ (8)

Where Δ_E represents the estimation energy, $r(X^-)$ is the radius of the halide, $r(Ag^+)$ is the ionic radius of a silver ion and the $a(AgX)$ is the unit cell constant.

The value of the indirect Γ- L transition of AgF (1.677 eV) differs little bit smaller than AgBr and AgCl (2.343 eV and 2.553 eV). However, the nature of this transition is the same (Wolan and Hoflund, 1998).

Figs. 1 and 2 shows the relationship between the calculated band structure and the density of states of AgBr, AgCl, and AgF. A comparison between Figs. 1 and 2 shows a good agreement with the experimental data for all cases in the first electronic transition of indirect $\Gamma - L$ type and the direct Γ transition see Table 1. It is known that he indirect transition energy of AgF is a bit smaller than AgCl because of small energy difference is
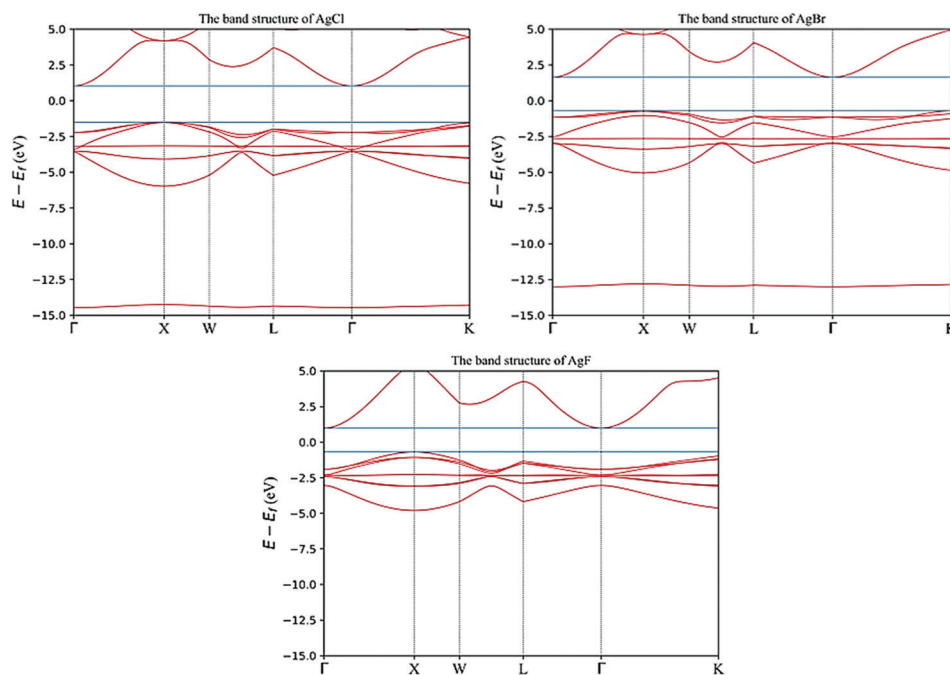
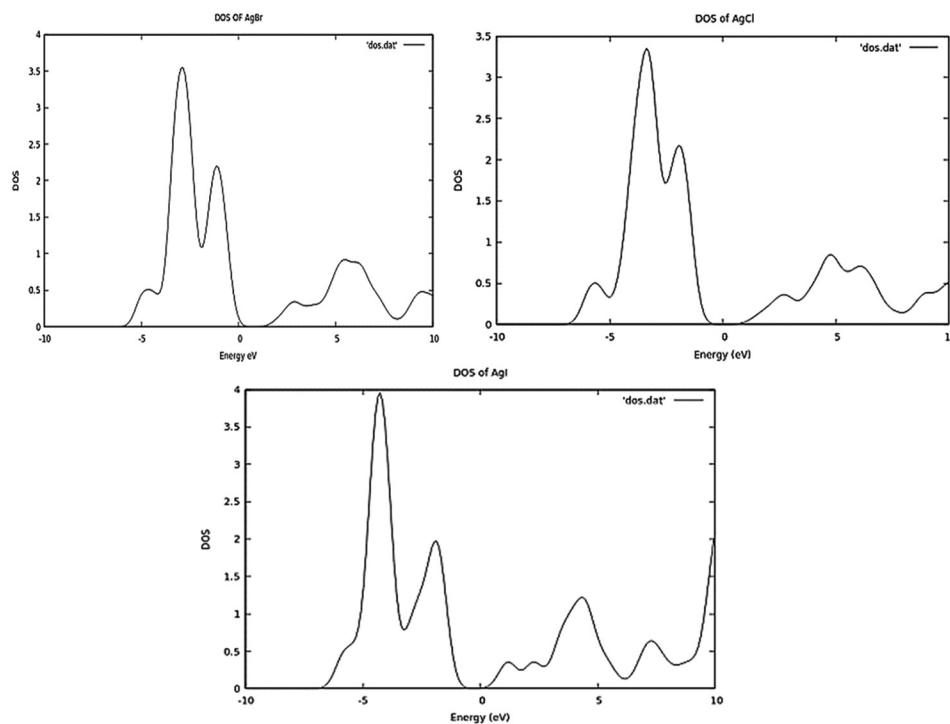Fig. 1. Band structure of AgCl, AgBr, and AgF (FCC).

Fig. 2. The density of states and the contribution of the 4-d (Ag) of the three silver halides.

due to the difference in the bounding energy due the interaction between the atoms (Glaus and Galzaferri, 1999). The broad bandgap is due to the strong surface plasmon resonance of the silver halides photosensitivity (Prachi et al., 2020).

Self-consistent local density calculations of the electronic structures of AgF, AgCl and AgBr are carried out by the tight binding linearized muffin-tin orbital-atomic sphere approximation (TB LMTO-ASA) method. The silver 4d orbital strongly hybridizes with the halogen p orbitals in the valence band and this plays a key role in the configuration of the total density of states (Gordienko, Zhuravlev and Poplavnoi, 1991). The relative position of the sharp peaks in the Ag d level and F, Cl, Br p level as well as the band gap values obtained in the total density of states of these silver halides are compared with the previous theoretical and experimental values. The silver halide AgX is used in

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TABLE I
EXPERIMENTAL AND THEORETICAL VALUES OF AGCL, AGBR, AND AGF.

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	Unit cell (A)	Ind. Transmission (eV)	Direct transmission (eV)	Unit cell (A)	Ind. Trans. Ev	Direct Trans. eV	Estimation ΔE	Unit cell (A)	Ind. Trans. (eV)	Direct Trans. (eV)	Estimation ΔE
	Experimental Data			Theoretical (Stephan and Calzaferri, 2003)				This work			
AgCl	5.54	2.8	5.15	5.46[a]	3.28	5.28	1.06	5.65	2.553	5.23	1.06
AgBr	5.77	3.25	4.29	5.63[a]	2.67	4.20	1.07	5.95	2.343	3.98	1.08
AgF	4.936	2.69	4.63	4.936	2.85	3.61	1.00	5.20	1.667	3.51	0.98

F. (Kirchhoff, Honender and Gilan, 1994)[a]

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TABLE II
THE BAND ENERGIES AT SYMMETRIC POINTS

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Γ	Γ_1	Γ_{12}		Γ'_{25}			Γ_{15}			Γ_1
	−14.4	−3.55	−3.55	−3.53	−3.53	−3.53	−2.22	−2.21	−2.21	1.23
L	−14.36	−5.22	−3.84	−3.84	−3.18	−3.18	−2.12	−1.98	−1.98	3.71
X	−14.26	−5.97	−4.08	−4.08	−3.16	−3.16	−1.53	−1.53	−1.51	4.19
W	−14.36	−5.21	−3.85	−3.84	−3.18	−3.18	−2.18	−1.87	−1.83	2.85
K	−14.29	−5.78	−4.03	−3.98	−3.19	−3.16	−1.78	−1.73	−1.56	4.43

photography because they are photosensitive to light and hyposolution because these halides decompose in to silver positive ion and negative halide ion (eq. 8). Silver is black in color, therefore it is sensitive to react with the light to form the halides. The hybridation comes from the transition of the exceeded electron from the 2, 3, and 4 p state halides to the positive silver halide to form the silver halides. Table 2 shows the band energies of AgCl in eV at symmetry points. For the zone center (Gamma), the wave function correspond each energy transforms according to the indicated irreducible representation.

Table 2 shows the band energies at symmetry points. For Γ as zone center, the 4d silver electron exhibits a threefold degenerate wave functions Γ'_{25} with defined energies of −3.53 eV and a twofold Γ_{12} wave functions with energies of −3.55 eV. The experimental binding energy (~3 eV) (Tejada et al., 1975) is little bit smaller than the theoretical one. There is some matching with the experimental value in the narrowest energy gap occurred in the Γ-L transition of the indirect energy gap.

The substantial degeneracies especially at Gamma point are due to the symmetry operations done by the point symmetry group. The size and morphologies of silver halides must be controlled when synthesizing these halides (Sasithac, Kowsalya and Yugang, 2017).

IV. CONCLUSIONS

This work gives some options to get information about these halides which can be applicable in several physical models. The simulated band gap of silver halides are in good agreement with most of the experimental and other theoretical result because of the flexibility of the code used here beside the well-chosen basis set to complete the simulation. Due to principle of used DFT theory, here we firstly tried to get a minimum energy ground state because this theory is based on the ground state energy which needs to find the minimum energy of AgX for different values of lattice constant, so

finding the lattice constant for the three silver halides were carried out by a series of test to choose the optimal lattice constant values. This study can be extended to simulate other physical properties such as optical, electrical, and mechanical properties.

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