
The Structural, Elastic, Electronic and Optical Properties of Cubic Perovskite SrVO₃ Compound: An Ab Initio Study

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Abstract: The structural, elastic, electronic and optical properties of cubic SrVO₃ perovskite have been investigated using the first principles pseudo-potential plane-wave (PP-PW) method based on the density functional theory (DFT), within the generalized gradient approximation (GGA). The calculated lattice parameters are in good agreement with the previous experimental and theoretical results. Using the energy-strain method, we obtained three independent elastic constants (C_{11} , C_{12} and C_{44}) and various elasticity parameters such as bulk modulus, Shear modulus, Young's modulus, B/G, Poisson's ratio and anisotropy factor. Our calculated results of elastic constants satisfy the structural stability criterion and the ductile/brittle of SrVO₃ is predicted by Pugh's criterion. The electronic band structure reveals metallic conductivity. Finally, the optical properties (reflectivity, dielectric function, refractive index, absorption spectrum, conductivity and energy loss spectrum) have been calculated and discussed.

Keywords: First Principle Calculations, Perovskite, Elastic Properties, Electronic Properties, Optical Properties

1. Introduction

Transition metal oxides (TMO) have always been great strong interest among the research community because of their remarkable physical properties [1-3]. Transition metal oxides are used in a wide variety of technological applications such as selective oxidation, selective reduction and dehydrogenation [4]. Cubic SrVO₃ perovskite materials possess unusual and useful electronic and magnetic properties. The TMO family SrVO₃ is the most widely studied material due to their cubic crystal structure at room temperature and high dielectric constant. It has numerous technological applications including catalysis, microelectronics, substrates for growth of high T_c superconductors, gas sensors, and thin films of cubic SrVO₃ perovskite. The density functional theory (DFT) is a power full tool for the description of ground state properties of metals, semiconductors and insulators, using this technique it is now possible to better understand the structural, elastic, electronic and optical properties of materials with good

accuracy.

A few numbers of theoretical and experimental works have been carried out on the structural and electronic properties of SrVO₃ compounds. I.R. Shein et al. [5] have performed a density functional study on structural, and electronic properties of cubic SrMO₃ (M = Ti, V, Zr and Nb) perovskite. The structural and electrical properties of SrVO₃ have been studied by B.K. Moon et al. [6]. The phase stability, structural, elastic and electronic properties of some mixed metal oxides of perovskite structure materials have been investigated by A.J. Smith et al. [7] using density functional theory (DFT) with the generalized gradient approximation (GGA).

It is thus evident from the above discussion that the majority of the cited works are dedicated to electronic properties and only a few of them discuss the elastic properties for perovskite crystal. To the best of our knowledge, no ab initio general potential investigation of the optical properties of the transition metal oxides has been reported. The main purpose of this work is to provide some additional information to the features of SrVO₃ by using

density functional theory. Therefore, in the present work, we have investigated the structural, elastic, electronic and optical properties of SrVO₃.

2. Computational Details

The calculations were performed using CASTEP computer program [8] based on the density functional theory (DFT) [9] together with the generalized gradient approximation (GGA) with the PBE exchange-correlation function [10]. The electronic wave functions are expanded in a plane wave basis set with an energy cut-off of 340 eV. The k- point sampling of the Brillouin zone was constructed using Monkhorst-Pack scheme [11] with used 4×4×4 grids in primitive cells of SrVO₃ compounds. The equilibrium crystal structures were obtained via geometry optimization in the Broyden-Fletcher-Goldfarb-Shanno (BFGS) minimization scheme [12]. The convergence thresholds of structural optimization are taken for the self-consistent calculations: (i) The criteria of convergence in the geometry optimization were set to 1.0×10^{-5} eV/atom for energy, (ii) the maximum ionic displacement is set to 1×10^{-3} Å (iii) the maximum stress is set to 0.05 GPa (iv) The maximum ionic Hellmann-feynman force is set to 0.03 eV/Å. These parameters are carefully tested and sufficient to lead to well-converged results.

3. Results and Discussions

3.1. Structural Properties

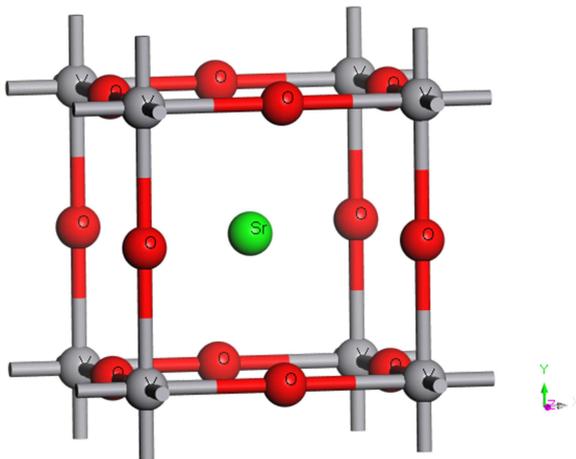


Fig. 1. The crystal structure of SrVO₃.

The cubic SrVO₃ perovskite belongs to cubic crystal structure with the space group Pm-3m (221). The value of equilibrium lattice parameter is 3.841 Å [5]. By minimizing the total energy the structure has been optimized as a function of normal pressure. The optimized crystal structure of SrVO₃ is shown in Fig. 1. In Table 1 the calculated values of the structural parameters of SrVO₃ have been shown along with the previous experimental and theoretical results. It can be seen that, Table 1 that our present theoretical results match well to both experimental and other theoretical results.

Table 1. The calculated equilibrium Lattice constant "a₀", unit cell volume "V₀" and bulk modulus "B₀" of SrVO₃ crystal.

| Properties | Expt. [23] | Other Calculation [5] | Present Calculation | Deviation from Expt. (%) |
|----------------------------------|------------|-----------------------|---------------------|--------------------------|
| a ₀ (Å) | 3.841 | 3.866 | 3.943 | 2.81 |
| V ₀ (Å ³) | - | - | 61.32 | - |
| B ₀ (GPa) | - | - | 122.41 | - |

From Table 1 one can see that the present calculated value of lattice constant is 3.943 Å which exhibits 2.81% deviation from the experimental value. Our calculated value is slightly different from the other theoretical value due to different calculation methods. The experimental data are measured at room temperature while our investigated data are simulated at 0 K. Perhaps this is the reason for the existing discrepancy between the present theoretical value and experimental value. Hence the above discussion indicates the reliability of our present first principle calculations of cubic SrVO₃ compound.

3.2. Elastic Properties

The elastic constants are important parameters that describe the response to an applied stress and various solid state phenomena, such as bonding characteristic between adjacent atomic planed, ductile/brittle, anisotropy character and structural stability. The elasticity of a cubic crystal is specified by the three independent elastic constants C₁₁, C₁₂ and C₄₄. In this work, the calculated elastic constants of SrVO₃ compound at zero pressure are presented in Table 2. It is well known that the mechanical stability criteria for cubic crystal are expressed as follows [13]

$$C_{11} > 0, C_{44} > 0, C_{11} - C_{12} > 0 \text{ and } C_{11} + 2C_{12} > 0$$

From Table 2, one can see that the elastic constants of SrVO₃ compound satisfy all of these conditions, suggesting that the structure of SrVO₃ compound is mechanically stable. The Cauchy pressure is defined as C₁₂ - C₄₄, which could be used to describe the angular character of atomic bonding in metals and compounds [14]. The negative value of Cauchy pressure indicates that the material is nonmetallic with directional bonding and if Cauchy pressure is positive, then the material is expected to be metallic [15]. From Table 2, it is evident that the value of the Cauchy pressure of SrVO₃ at an ambient condition is negative indicates the nonmetallic behavior of this compound. But this result is totally opposite to the result getting from the band structure diagram. The explanation for this contradiction is currently unknown and further investigation is expected in future. From results of the calculated elastic constants, the mechanical parameters such as bulk modulus B, Shear modulus G, Young's modulus $E = 9BG/(3B+G)$ and poisson's ratio $\nu = (3B-2G)/(2(3B+G))$ are determined by using the Voigt-Reuss-Hill approximation [16]. The zener elastic anisotropy of crystal, defined by the ratio $A = 2C_{44}/(C_{11} - C_{12})$ [17]. As shown in Table 1, that the calculated anisotropy factor A is larger than unity, which indicates that, the SrVO₃ compound is elastically anisotropic material. The poisson's ratio is used to reflect the stability of the material. Bigger the Poisson's ratio betters the plasticity.

Poisson's ratio provides useful information about the characteristic of the bonding forces. Poisson's ratio of SrVO₃ is 0.22 at 0 GPa, which means that interatomic forces within SrVO₃ are noncentral, since Poisson's ratio $\nu = 0.25$ is the lower limit for central force solids and the upper limit is $\nu = 0.50$ [18].

Another index to explain the ductility and brittleness of a material is Pugh's ratio is defined as B/G [19]. A material behaves in a brittle manner, if $B/G < 1.75$, otherwise it should be ductile. From Table 2, it is evident that this compound is brittle at ambient pressure. Another parameter indicating, the material is expected to be ductile, if the value of Cauchy pressure is positive, on the other hand, if its value is negative, the material is brittle. From Table 2, it can be seen that the value of Cauchy pressure is negative indicates that the studied compound is brittle.

Table 2. Calculated elastic constants C_{ij} (GPa), Cauchy pressure ($C_{12} - C_{44}$), bulk modulus B (GPa), shear modulus G (GPa), Young's modulus E (GPa), Poisson's ratio ν , elastic anisotropic factor A for SrVO₃ crystal at $P = 0$ GPa and $T = 0$ K.

| C_{11} | C_{12} | C_{44} | B | G | B/G | E | ν | A | $C_{12} - C_{44}$ |
|---------------------|--------------------|---------------------|--------------------|-------|-------|--------|-------------------|------|-------------------|
| 212.95 | 77.13 | 94.99 | 122.40 | 83.04 | 1.47 | 203.17 | 0.22 | 1.39 | -17.86 |
| 269.88 ^a | 77.13 ^a | 113.63 ^a | 181.0 ^a | 66.27 | -- | -- | 0.21 ^a | -- | -- |

^a Ref. [5]

3.3. Electronic Properties

The study of the density of states is crucial in the analysis of the physical properties of cubic SrVO₃ crystal. In order to know the details bonding nature of SrVO₃ compound, we illustrate the investigated the total density of states (TDOS) and partial density of states (PDOS) at normal pressure as shown in Fig. 3. To know about the metallic nature of SrVO₃ the electronic band structures along the high symmetry directions in the Brillouin zones have been calculated and is shown in Fig. 2. From the band structure diagram as shown in Fig. 2, it is noticed that SrVO₃ exhibits metallic nature since a number of conduction and valence bands are overlapping at the Fermi level.

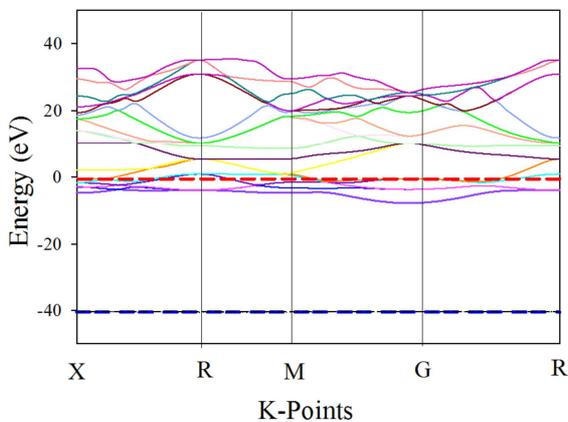


Fig. 2. Electronic band structure of SrVO₃ along high symmetry direction in the Brillouin zones.

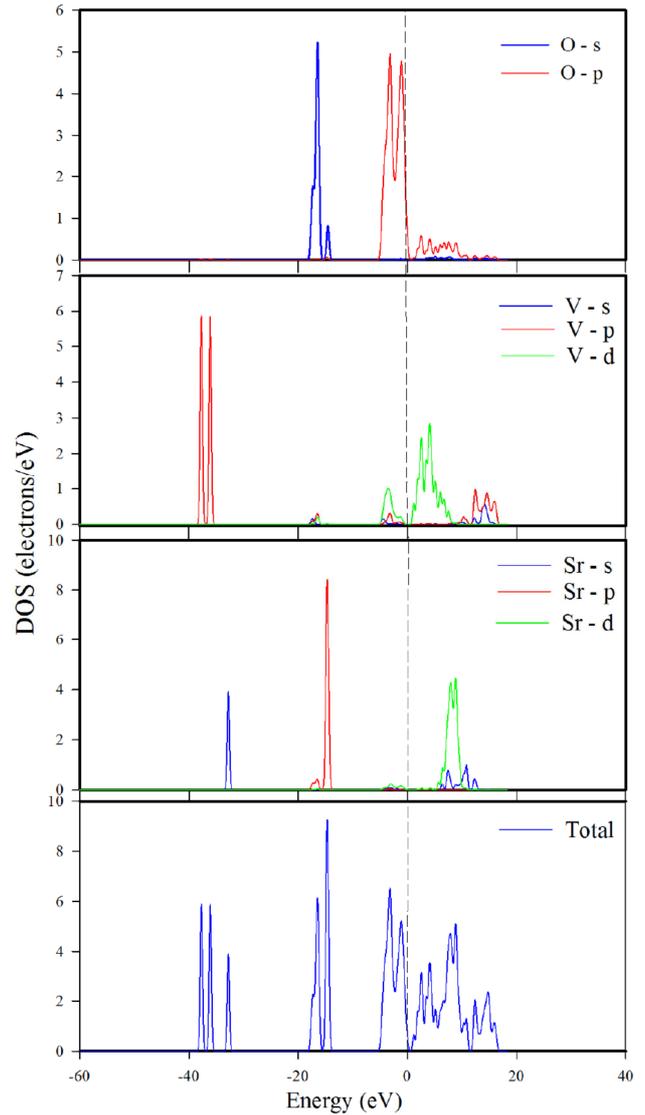


Fig. 3. The partial and total density of states of SrVO₃.

For further understanding about the bonding property of SrVO₃, we have run further investigations on Mulliken overlap population [20]. Mulliken overlap population is a great quantitative criterion for investigating the covalent and ionic nature of bonds. In Table 3, we have listed the atomic Mulliken population of SrVO₃ compound. A high value of the bond population indicates a covalent bond, whereas a low value denotes the ionic bonds. A value of zero indicates a perfectly ionic bond and the values greater than zero indicate the increasing levels of covalency [8]. From Table 3, it can be concluded that O-V bond exhibits some covalent character and the O-Sr, O-O bonds shows ionicity.

Table 3. Mulliken electronic populations of SrVO₃.

| Species | s | p | d | Total | Charge | Bond Population | Lengths |
|---------|------|------|------|-------|--------|-----------------|---------|
| O | 1.85 | 4.85 | 0.00 | 6.70 | -0.70 | O-V 0.77 | 1.971 |
| V | 2.30 | 6.61 | 3.33 | 12.24 | 0.76 | O-Sr -0.15 | 2.788 |
| Sr | 2.06 | 5.99 | 0.59 | 8.65 | 1.35 | O-O -0.11 | 2.788 |

3.4. Optical Properties

The study of the optical properties helps to give a better understanding of the electronic structure of materials. The frequency dependent dielectric function $\epsilon(\omega) = \epsilon_1(\omega) + i\epsilon_2(\omega)$ is used to determine the optical properties of SrVO₃. Where $\epsilon_2(\omega)$ is the imaginary part which is obtained from the momentum matrix elements between the filled and the unfilled electronic states and calculated using the below equation [21] –

$$\epsilon_2(\omega) = \frac{2e^2\pi}{\Omega\epsilon_0} \sum_{k,v,c} |\psi_k^c| u.r |\psi_k^v|^2 \delta(E_k^c - E_k^v - E)$$

Where, u is defined as the polarization of the incident electric field, ω is defined as the frequency of light, e is the charge of electron, ψ_k^c is the conduction band wave function and ψ_k^v is the valence band wave function at K respectively. The Kramers-Kronig transform is used to derive the real part. From Eqs. 49 to 54 in ref. [21] are used to determine the all other optical constants. Fig. 4 and Fig. 5 represent the optical functions of SrVO₃ investigated for photon energies up to 80 eV. 0.5 eV Gaussain smearing is used for all calculations. This smears out the Fermi level, so that k-points will be more effective on the Fermi surface.

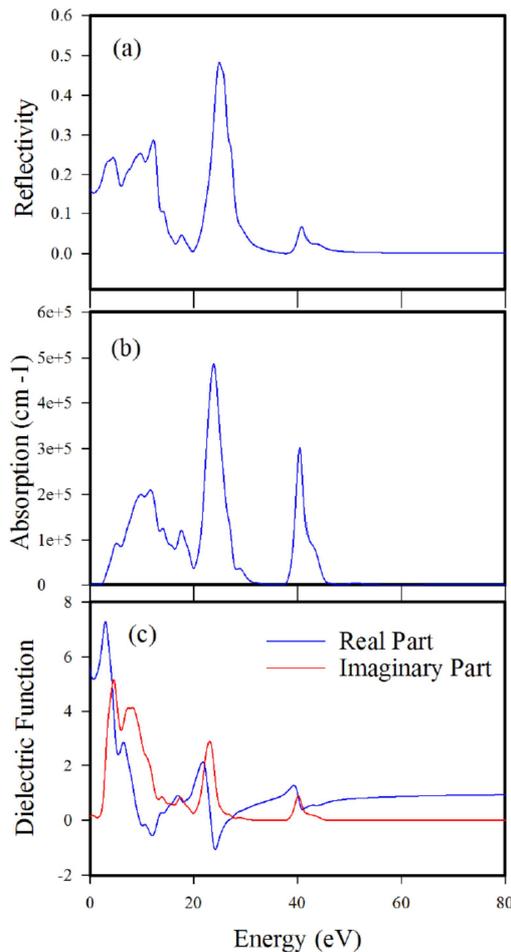


Fig. 4. The optical functions (a) reflectivity, (b) absorption, (c) dielectric function of SrVO₃.

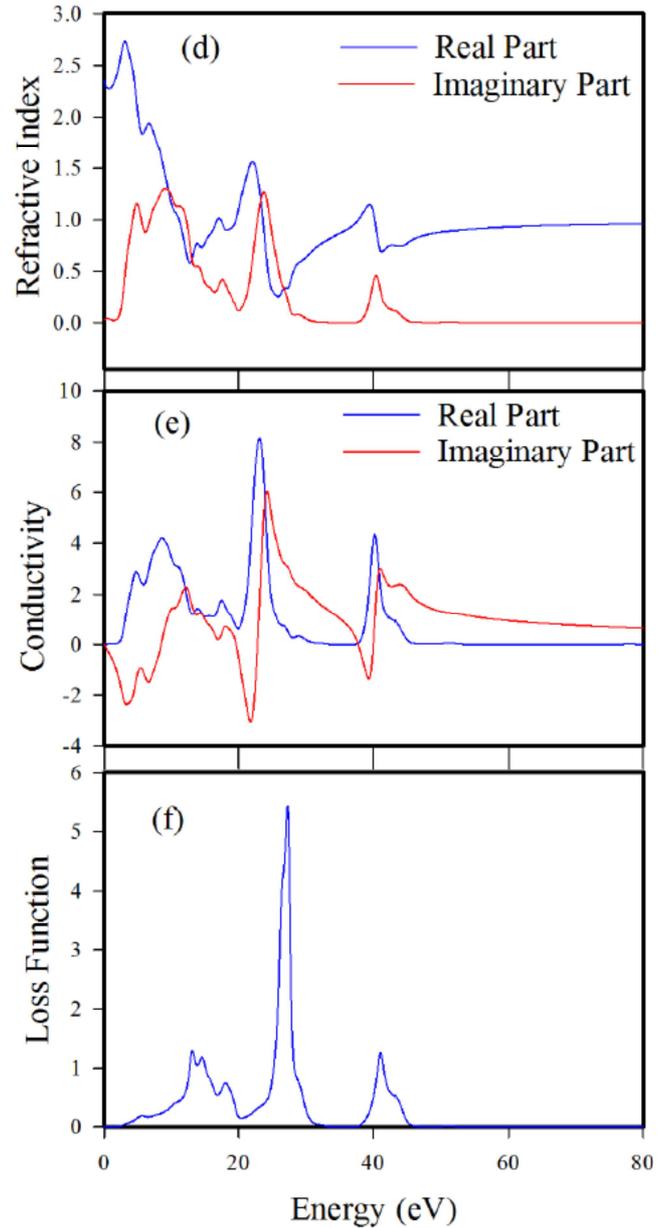


Fig. 5. The optical functions (d) refractive index, (e) conductivity, and (f) loss function of SrVO₃.

The reflectivity spectra as a function of photon energy as shown in Fig. 4(a). The reflectivity spectra of SrVO₃, shows promise as good coating materials between 20 eV and 28.5 eV regions. The absorption coefficient provides data about optimum solar energy conversion efficiency and it indicates how for light of a specific energy can penetrate into the material before being absorbed. The absorption coefficient of SrVO₃ is shown in Fig. 4(b), from which we see that the highest peak located at 23.5 eV. This value indicates that SrVO₃ has good absorption coefficient in the ultraviolet region. The dielectric function of SrVO₃ is represented in Fig. 4(c) as a function of photon energy. The dielectric function describes what an electric field such as an oscillating light wave does to material. It describes the polarization and absorption properties of the materials.

Materials with high dielectric constants are useful in the manufacture of high value capacitors. Fig. 5(d) shows the diagram of refractive index of SrVO₃. Fig. 5(e) illustrates the conductivity spectra of SrVO₃. From this figure we see that photoconductivity starts with zero photon energy, which indicates the metallic nature of SrVO₃. The energy loss function is an important optical parameter to describe the energy loss of a fast electron traversing the material and is large at the plasma frequency [22]. Fig. 5(f) represents the energy loss spectrum of SrVO₃ as a function of photon energy. We found the prominent peak at about 28 eV, at which the reflectance is rapidly diminished.

4. Conclusions

In this paper, we have studied the structural, elastic, electronic and optical properties of cubic SrVO₃ by using the generalized gradient approximation (GGA). We have just run our investigation using GGA-PBE. The calculated lattice parameters show good agreement with the experimental and other theoretical values.

The elastic constants C_{11} , C_{12} and C_{44} , and related mechanical parameters such as bulk modulus B , shear modulus G , Young's modulus E , and Poisson's ratio ν are calculated. The SrVO₃ compound is mechanical stable according to the elastic stability criteria. The zener factor A , the B/G ratio and Cauchy pressure ($C_{11} - C_{44}$) are also calculated. The values of the ratio B/G and Cauchy pressure show a brittle behavior for the SrVO₃ compound.

The study of electronic properties shows that the compound under study is metallic in nature. The investigation of DOS shows that the major contribution near the Fermi level comes from V-d states. Further investigation on the Mulliken overlap population indicates that the ionic nature is dominant in SrVO₃ compound.

For the first time we have investigated the optical properties, e.g., absorption, conductivity, reflectivity, refractive index, energy loss spectrum and dielectric function of SrVO₃ cubic perovskite. The study on optical properties of SrVO₃ exhibits that the reflectivity is high in the ultraviolet region up to 73 eV. The absorption coefficient of SrVO₃ is good in the ultraviolet region. However we expect that this present study will motivate to experimental investigation on electronic and optical properties of cubic SrVO₃.

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