Alkaline-Earth Metal Effects on Physical Properties of Ferromagnetic AVO₃ (A = Ba, Sr, Ca, and Mg): Density Functional Theory Insights

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ABSTRACT: The effects of alkaline-earth metals on electronic, optical, thermodynamic, and physical properties of ferromagnetic AVO₃ (A = Ba, Sr, Ca, and Mg) have been investigated by first-principles calculations within the GGA+U formalism based on density functional theory. The optimized structural parameters are in good agreement with the available experimental results that evaluate the reliability of our calculations. The cell and mechanical stability is discussed using the formation energy and Born stability criteria, respectively. The mechanical behaviors of AVO₃ are discussed on the basis of the results of elastic constants, elastic moduli, Peierls stress, and Vickers hardness. The nature of the ductile−brittle transition of AVO₃ compounds was confirmed by the values of Pugh’s ratio, Poisson’s ratio, and Cauchy pressure. The electronic band structures, as well as density of states, reveal the half-metallic behavior of BaVO₃ and SrVO₃. However, CaVO₃ and MgVO₃ exhibit spin-gapless and magnetic semiconductor characteristics, respectively. The microscopic origin of the transition from the half-metallic to semiconductor nature of AVO₃ is rationalized using electronic properties. The presence of covalent, ionic, and metallic bonds in AVO₃ compounds is found by the analysis of bonding properties. The single-band nature of half-metallic AVO₃ is seen by observing hole-like Fermi surfaces in this study. Furthermore, the various thermodynamic and optical properties are calculated and analyzed. The refractive index suggests that AVO₃ could be a potential candidate for applications to high-density optical data storage devices.

1. INTRODUCTION

The understanding of ABO₃-type oxide perovskites is crucial not only due to their structures and properties being modified by the exchange of distinct elements into their crystallographic equivalent sites but also for investigating phase transitions. This type of material is also fundamentally interesting and bears technological importance because of its ferroelectric, multiferroic, magnetic, and superconducting properties, which originate from an interplay between the chemical composition and the structure type. Recently, the study of AVO₃ (A = Ba, Sr, Ca, and Mg) has been given much attention because of its strong couplings between the lattice degrees of freedom and spin, which makes them a potential candidate for the application to spintronics devices. It has been found that few atoms at the A site in AVO₃, e.g., PbVO₃, showed antiferromagnetic ordering with large spontaneous polarization. Belik et al. also reported the insulator to metal transformation, induced by crystal symmetry variations from the tetragonal to cubic phase in PbVO₃.

AVO₃ (A = Ba, Sr, Ca, and Mg) have been synthesized by using high-temperature and high-pressure (HTHP) conditions for investigating their structural and relevant properties. BaVO₃ showed a polycrystalline phase with a cubic perovskite structure under high pressures, and it should be noted that Ba₃(VO₄)₂ was formed instead of BaVO₃ when either the pressure or temperature was insufficient. Notably, SrVO₃ and CaVO₃ have correlated Mott conductors in which SrVO₃ is cubic perovskite, and their oxygen nonstoichiometric effects on the structures and electronic states are investigated extensively. Strontium vanadate has a simple cubic perovskite structure with a = 3.842 Å that exhibits Pauli paramagnetic and metallic characteristics near room temperature as well. Additionally, the dielectric function, the band structure, the Fermi surface, and interband optical transitions of the SrVO₃ transparent conducting thin film have also been analyzed from the first-principles study. Moreover, this material has attracted great attention as a potential oxide...
electrical conductor.\textsuperscript{18,19} However, stoichiometric CaVO\textsubscript{3} belongs to the orthorhombic phase, while nonstoichiometric CaVO\textsubscript{3−δ} (0.04 < δ < 0.08) and CaVO\textsubscript{3+δ} (δ = 0.20) show cubic and monoclinic phases, respectively.\textsuperscript{14,15} In addition, the slightly oxidized CaVO\textsubscript{3+δ} exhibits insulating behavior without any significant structural changes.\textsuperscript{27} At ambient pressure, Chamberland \textit{et al.} reported the orthorhombic crystal structure of MgVO\textsubscript{3}, whereas the high-pressure adjustment of MgVO\textsubscript{3} exhibited a triclinic structure.\textsuperscript{28} The electronic band structure with various spin arrangements for MgVO\textsubscript{3} showed paramagnetic as well as magnetic solutions with ferro- and antiferromagnetic ordering.\textsuperscript{23,29} Between them, the paramagnetic solution has metallic behavior, whereas the band splits into two in the magnetic solutions with an insulator gap in ferro- and antiferromagnetic states.\textsuperscript{23} Hence, with the substitution of distinct A site cations, a perovskite may show various stable phases and correspondingly diverse material peculiarities. Therefore, it is interesting to discover the electronic, optical, and diverse physical properties of AVO\textsubscript{3} perovskites, where A is a divalent cation.

Nowadays, the cubic phase of oxide perovskite materials is an extensive research area for the proper explanation of electronic, elastic, vibrational, thermodynamic, and optical properties for emergent applications. Recently, Kamruzzaman \textit{et al.}\textsuperscript{30} reported a comparative study on the cubic phases of ATiO\textsubscript{3} (A = Ba, Ca, Pb, and Sr) by first-principles calculations. The first-principles calculations on the cubic phase of simple and double-perovskite Bi oxide magnetic materials, which exhibited superconductivity, envisage different interesting physical properties including electronic, mechanical, and thermodynamic properties as well.\textsuperscript{3,25,26} The cubic perovskite structures of AVO\textsubscript{3} (A = Ba, Sr, Ca, and Mg) are our point of interest in the present investigation. The cubic phase with \textit{Pm\textbar m\textbar a} symmetry of SrVO\textsubscript{3} and BaVO\textsubscript{3} was reported experimentally,\textsuperscript{12,13} whereas CaVO\textsubscript{3} and MgVO\textsubscript{3} show an intrinsically orthorhombic phase.\textsuperscript{14,15} The cubic phase of CaVO\textsubscript{3} and MgVO\textsubscript{3} may be comprehended by using specifically designed growth conditions similar to those implemented for achieving hexagonal Si.\textsuperscript{27} Rashid \textit{et al.}\textsuperscript{28} reported metallic behavior in both spin channels of cubic BaVO\textsubscript{3} and LaVO\textsubscript{3} using the GGA-PBE exchange–correlation, while the utilization of the mbJ scheme explicated a clear half-metallic ferromagnetic behavior. They discussed the electronic and thermoelectric properties of BaVO\textsubscript{3} and LaVO\textsubscript{3}. The electronic, magnetic, and optical properties in the low-energy range (0−15 eV) of cubic AVO\textsubscript{3} (Ba, Sr, and Ca) were studied by first-principles calculations.\textsuperscript{29} However, extensive studies on the alkaline-earth metal’s effects on physical properties (elastic constants, elastic moduli, Peierls stress, Pugh’s and Poisson’s ratio, Cauchy pressure, and Vickers hardness), the Fermi surface, electronic charge density, and population analysis are rather scarce, which are crucial for accelerating the applications and understanding of these material systems precisely.

In this study, we have investigated the structural, physical (elastic constants, Young’s shear, and bulk moduli, Pugh’s and Poisson’s ratio, Cauchy pressure, Peierls stress, and Vickers hardness), electronic (the band structure, charge density map, DOS, and Fermi surface), optical (the dielectric function, photoconductivity, refractive index, reflectance, and absorbance), population analysis, and thermodynamic properties (melting temperature, Debye temperature, and minimum thermal conductivity) considering the cubic phase of ferromagnetic AVO\textsubscript{3} by altering cations Ba, Sr, Ca, and Mg employing density functional theory (DFT)-based CASTEP code. The possibility of applications to high-density optical data storage devices of AVO\textsubscript{3} has been discussed on the basis of observed optical properties.

2. COMPUTATIONAL METHODS

The present calculations based on density functional theory (DFT)\textsuperscript{30,31} were carried out with the Cambridge Serial Total Energy Package (CASTEP) code\textsuperscript{32} utilizing the GGA+U parameterization scheme. The spin-polarized scheme using formal spin as the initial state with charge neutrality conditions was implemented in the relatively high-level computation GGA + U method. The default value of Hubbard $U = 2.5$ eV for V 3d was set for computations in this study. The ultrasoft pseudopotential formalism of the Vanderbilt type\textsuperscript{13} was utilized for all atoms to simulate the interactions of valence electrons with ion cores. The choice of exchange–correlation functionals (XCs) was regarded as a crucial parameter for first-principles calculations. Therefore, geometry optimization of the cubic structure of BaVO\textsubscript{3} with \textit{Pm\textbar m\textbar a} symmetry with fully relaxed structures was performed by the Broyden–Fletcher–Goldfarb–Shannon (BFGS) algorithm\textsuperscript{34} using various XCs to search the ground state to obtain the best lattice parameters and compare them with the available experimental ones. The XC that induced the best results for BaVO\textsubscript{3} was used to calculate all properties of AVO\textsubscript{3} (A = Ba, Sr, Ca, and Mg) by altering the A cations. The electronic wave function with a cutoff energy of 700 eV was used for all calculations of cubic AVO\textsubscript{3} with a ferromagnetic (FM) configuration because the FM state was relatively more stable than the antiferromagnetic (AFM) state.\textsuperscript{35} According to the Monkhorst–Pack scheme,\textsuperscript{36} 12 × 12 × 12 k-point grids were employed for sampling the irreducible Brillouin zone. In the present calculations, the convergence tolerances for geometry optimization were set to be $1 \times 10^{-6}$ eV/atom (total energy), 0.03 eV/Å (maximum force on atoms), 0.001 Å (maximum atom displacements), and 0.05 GPa (maximum stress).

3. RESULTS AND DISCUSSION

3.1. Structural Parameters and Cell Stability. The oxide perovskites AVO\textsubscript{3} (A = Ba and Sr) belong to the cubic phase with \textit{Pm\textbar m\textbar a} (no. 221) symmetry consisting of an A atom at the corner, V in the body center, and O at the face center of the cube.\textsuperscript{12,13} The cubic phase of nonstoichiometric CaVO\textsubscript{3−δ} (0.04 < δ < 0.08) was reported experimentally by Ueda,\textsuperscript{14} while stoichiometric CaVO\textsubscript{3} and MgVO\textsubscript{3} showed an orthorhombic phase.\textsuperscript{14,15} To realize the cubic phase of CaVO\textsubscript{3} and MgVO\textsubscript{3} specifically designed growth schemes similar to those implemented for observing hexagonal Si are necessary.\textsuperscript{27} First, the crystal structure of BaVO\textsubscript{3} was sketched using the available refinement data\textsuperscript{15} in this study. After that, the structures were absolutely relaxed with the lattice parameters and internal coordinates in order to optimize the geometry by swapping A site cations. The crystal structures of the cubic AVO\textsubscript{3} (A = Ba, Sr, Ca, and Mg) system are depicted in Figure 1. The optimized lattice parameters of AVO\textsubscript{3} substances, both theoretical and experimental data, are summarized in Table 1. The calculated values of lattice parameters match reasonably with the experimental results,\textsuperscript{12−14} and the relation is noted as follows: $a(\text{BaVO}_3) > a(\text{SrVO}_3) > a(\text{CaVO}_3) > a(\text{MgVO}_3)$. The resultant interatomic distance decreases with decreasing atomic radii.
from the bottom to top in a group, which results in a decreasing trend in lattice parameters. Interestingly, these consequences are similar to those observed in ATiO$_3$ (A = Ba, Ca, Pb, and Sr) compounds.\textsuperscript{24} Moreover, the chemical stability of AVO$_3$ can be confirmed by analyzing their formation energies. The formation energy ($\Delta E_f$) is approximated by the subtraction of the total energies of pure constituent atoms from the total energy of the materials in their stable structures. The magnitude of $\Delta E_f$ of AVO$_3$ is estimated by the following expression:\textsuperscript{36}

$$\Delta E_f(\text{AVO}_3) = \left[ E_{\text{tot}}(\text{AVO}_3)_{\text{fu}} - E_{\text{f}}(A) - E_{\text{f}}(V) - 3E_{\text{f}}(O) \right]$$

(1)

Here, $E_{\text{tot}}(\text{AVO}_3)_{\text{fu}}$ represents the total energy per formula unit and is given by $E_{\text{tot}}(\text{AVO}_3)_{\text{fu}} = 1/N[E_{\text{tot}}(\text{AVO}_3)_{\text{cell}}]$, where $N$ denotes the number of formula units per unit cell, $E_{\text{f}}(A)$, $E_{\text{f}}(V)$, and $E_{\text{f}}(O)$ are the total energies per atom of the pure elements A, V, and O, respectively, in their ground-state solid phases. So, $\Delta E_f$ per atom = $\Delta E_f(\text{AVO}_3)_{\text{fu}}/N$, where $N_f$ denotes the total number of atoms in one formula unit. The calculated formation energies of ferromagnetic AVO$_3$ are also displayed in Table 2. It is seen from Table 2 that the energies of AVO$_3$ are stable. The chemical stability of solids against the (100) uniaxial strain of the (100) plane can be signified by the value of $C_{11}$. The elasticity in shape is given by the elastic constants $C_{12}$ and $C_{44}$, and these constants describe the elasticity in length along the $C_{11}$ direction and $C_{12}$ indicates the pure shear stress in the (110) plane along the (110) direction. As can be seen in Table 3, CaVO$_3$ has the largest value of $C_{11}$ compared to others. It is worth noting that the calculated value of $C_{11}$ for all perovskites is higher than $C_{12}$, indicating that the bonding strength along the (100) direction is higher than that along the (110) directions in AVO$_3$. This result indicates that the elasticity in length is stiffer than the elasticity in shape. The Kleinman parameter ($\xi$) measures the ease of bond bending to bond stretching. In general, the value of $\xi$ can be between 0 and 1 ($0 \leq \xi \leq 1$) and is estimated using the following expression:\textsuperscript{39}

$$\xi = \frac{C_{11} + 8C_{12}}{7C_{11} + 2C_{12}}$$

(2)

Kleinman reported that the upper limit corresponds to a minimized bond bending term and the lower limit corresponds to a minimized bond stretching term.\textsuperscript{40} The calculated value of $\xi$ for AVO$_3$ compounds is shown in Table 2. The estimated value of $\xi$ of ~0.50 for AVO$_3$ compounds is in good agreement with the previously reported value of $\xi$ of ~0.55 for perovskite LaAlO$_3$.\textsuperscript{41} The calculated value of $\xi$ suggests the strong bonding nature of AVO$_3$, which is dominated by the bond bending compared to the bond stretching.

The various elastic properties such as the bulk modulus, $B$, shear modulus, $G$, Young’s modulus, $E$, and Poisson’s ratio, $\nu$, are calculated from the single-crystal zero-pressure elastic constants using well-known relationships.\textsuperscript{42,43} The calculated elastic parameters are shown in Table 2. The constituent constants $B$, $C_{11} - C_{12}$, and $C_{44}$ be positive. Following these stability conditions, the calculated elastic constants are presented in Table 2. Therefore, the chosen cubic phase of AVO$_3$ in this investigation is mechanically stable. The tendency of a solid to deform non-permanently in diverse directions with applied stress is measured by its elastic property. The elastic constants provide information about the bonding behavior of solids as well. The elastic constant $C_{11}$ gives the elasticity along the axial length. So, the elastic stiffness of solids against the (100) uniaxial strain of the (100) plane can be signified by the value of $C_{11}$. The elasticity in shape is given by the elastic constants $C_{12}$ and $C_{44}$, and these constants describe the elasticity in length along the $C_{11}$ direction and $C_{12}$ indicates the pure shear stress in the (110) plane along the (110) direction. As can be seen in Table 3, CaVO$_3$ has the largest value of $C_{11}$ compared to others. It is worth noting that the calculated value of $C_{11}$ for all perovskites is higher than $C_{12}$, indicating that the bonding strength along the (100) direction is higher than that along the (110) directions in AVO$_3$. This result indicates that the elasticity in length is stiffer than the elasticity in shape. The Kleinman parameter ($\xi$) measures the ease of bond bending to bond stretching. In general, the value of $\xi$ can be between 0 and 1 ($0 \leq \xi \leq 1$) and is estimated using the following expression:\textsuperscript{39}

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### Table 1. The Optimized Lattice Parameter, $a$ (Å), of BaVO$_3$ with Different XCs and Compared with the Available Experimental Results

| exchange–correlation functions (XCs) | PBE | RPBE | PW91 | WC | PBEsol | expt$^4$ |
|-------------------------------------|-----|------|------|----|--------|--------|
| lattice parameter                   | 3.97846 | 4.01721 | 3.97463 | 3.92674 | 3.92391 | 3.94288 |

$^4$Ref 12.
atom’s average bond strength for a given solid is assessed by the bulk modulus. Recently, Rahaman et al. found the moderate bonding strength in LiCuBiO3 by observing the bulk modulus of 101 GPa. However, Nasir et al. reported the strong bonding in ScIrP and ScRhP by the bulk moduli of 190 and 171 GPa, respectively. Thus, the calculated values of \( B \) in the range of 177–198 GPa (Table 2) may imply the strong bonding strength of atoms involved in AVO3. It is also seen from Table 2 that the bulk modulus improves by varying cations from Ba to Mg. The cationic size decreases the compressibility of the compounds, making the solid dense that enhances the bulk modulus of AVO3. The bond strength of atoms also gives the required resistance to volume deformation under external pressure. In contrast, the \( G \) evaluates the change of shape in a solid, which exhibits a crucial relationship with the hardness of materials. The material becomes more rigid when the value of \( G \) becomes greater. The Young’s modulus, \( E \), exerts an influence on the thermal shock resistance of solid matter. The critical thermal shock coefficient varies inversely with respect to \( E \). The greater the value of the thermal shock coefficient, the better the thermal shock resistance. A material is chosen as a thermal barrier coating (TBC) substance based on thermal shock resistance. Notably, AVO3 has a comparatively higher Young’s modulus, and hence, it might not be suitable as a TBC material. However, the calculated value of \( G \) (197–287 GPa) indicates that AVO3 is moderately stiff. The moduli of elasticity such as \( G \), \( B \), and \( E \) are not only useful to explain the mechanical properties of solids but also effective to estimate the hardness of materials. \( C_{44} \) is the best one to predict the hardness of solids among the observed elastic constants. Moreover, the shear modulus (\( G \)) is considered as the best hardness predictor among the moduli of elasticity as well. It is evident from Table 3 that BaVO3 is harder than the rest of the compounds in this study. These statements may be strengthened by the calculations of hardness by Chen’s formula, which can be expressed as \( H_v = 2(k^2G)^{0.585} - 3 \), where \( k \) is the Pugh ratio (\( G/B \)). The estimated values of \( H_v \) are displayed in Table 3 and found to be consistent with the earlier predictions based on the values of \( C_{44} \) and \( G \). Mazhnik and Oganov reveal conducive agreement between the experimental and theoretical values of hardness of different materials calculated using Chen’s formula. It is well-established that diamond (\( H_v = 96 \text{ GPa} \)), BC3N (\( H_v = 76 \text{ GPa} \)), and BC1 (\( H_v = 71 \text{ GPa} \)) are widely used as superhard materials. Thus, the much lower harness of AVO3 in comparison with superhard materials confirms that the studied compounds do not belong to superhard materials. However, the value of \( H_v \) of half-metallic BaVO3, SrVO3, and CaVO3 is comparable with hard refractory materials NbC (\( H_v = 16.0 \text{ GPa} \)), GaN (\( H_v = 15.1 \text{ GPa} \)), and GaN (\( H_v = 12.0 \text{ GPa} \)), respectively, whereas the \( H_v \) value of MgVO3 is comparable with the semiconductor AlAs (\( H_v = 5.0 \text{ GPa} \)). The relatively large value of hardness denotes that BaVO3, SrVO3, and CaVO3 are not machinable, whereas MgVO3 is machinable by conventional cutting machines.

Furthermore, the study of failure modes, i.e., the ductile or brittle nature of a material, is technologically very important. For most practical situations, a material may be classified as either brittle or ductile. Figure 2 shows the graphical representation of ductile/brittle behavior of AVO3 (A = Ba, Sr, Ca, and Mg). The horizontal dashed lines indicate the ductile–brittle transition line.

Table 3. The Elastic Constants, \( C_{ij} \) (GPa), Bulk Moduli, \( B \) (GPa), Shear Moduli, \( G \) (GPa), Young’s Moduli, \( E \) (GPa), the Kleinman Parameter, \( \xi \), the Burgers Vector, \( b \) (Å), the Interlayer Distance, \( d \) (Å), and Peierls Stress, \( \sigma_p \) (GPa), of AVO3 Compounds

| Compounds | \( C_{11} \) | \( C_{12} \) | \( C_{14} \) | \( B \) | \( G \) | \( E \) | \( \xi \) | \( b \) | \( d \) | \( \sigma_p \) | \( H_v \) |
|-----------|---------------|---------------|---------------|-----|-----|-----|-------|---|---|-----------|-------|
| BaVO3     | 300           | 116           | 134           | 177 | 115 | 283 | 0.527 | 3.927 | 1.963 | 2.489 | 16.4  |
| SrVO3     | 335           | 113           | 118           | 187 | 115 | 287 | 0.482 | 3.830 | 1.915 | 2.380 | 15.2  |
| CaVO3     | 351           | 113           | 98            | 192 | 106 | 268 | 0.468 | 3.774 | 1.887 | 1.985 | 12.3  |
| MgVO3     | 345           | 124           | 56            | 198 | 74  | 197 | 0.502 | 3.741 | 1.871 | 0.990 | 4.9   |

Figure 2. (Color online) Calculated Pugh’s ratio (\( G/B \)), Poisson’s ratio (\( \nu \)), and Cauchy pressure (\( C_{12}−C_{66} \)) showing the graphical representation of ductile/brittle behavior of AVO3 (A = Ba, Sr, Ca, and Mg). The horizontal dashed lines indicate the ductile–brittle transition line.
edge to accelerate dislocation in a glide plane of the synthesized cubic perovskite crystals as well. The Peierls stress can be estimated using the shear modulus (\(G\)) and the Poisson ratio (\(\nu\)) as follows:\(^{53}\)

\[
\sigma_p = \frac{G}{1 - \nu} \exp\left[-\frac{2\pi d}{b(1 - \nu)}\right]
\]  

(3)

Herein, \(d\) and \(b\) denote the interlayer distance between the glide planes and the Burgers vector, respectively. The calculated interlayer distance (\(d\)), the Burgers vector (\(b\)), and the resulting Peierls stress (\(\sigma_p\)) of AVO\(_3\) are presented in Table 3. It is seen from Table 3 that the values of \(\sigma_p\) decrease as we follow the sequence Ba\(\rightarrow\)Sr\(\rightarrow\)Ca\(\rightarrow\)Mg. The lowest and highest values of estimated Peierls stress are 0.990 and 2.489 GPa for MgVO\(_3\) and BaVO\(_3\), respectively. The \(\sigma_p\) values of BaVO\(_3\), SrVO\(_3\), and CaVO\(_3\) are comparable to the reported double MgVO\(_3\) and BaVO\(_3\), respectively, and also a negligible energy gap (\(\sim\)0.03 eV) between the valence and conduction bands is observed (Figure 5c), which appears owing to the existence of vanadium cations in the studied perovskites. It is seen from Figure 5 that the valence and conduction bands of SrVO\(_3\), CaVO\(_3\), and MgVO\(_3\) appreciably overlap with each other and also a negligible energy gap (\(\sim\)0.03 eV) between the valence and conduction bands is observed (Figure 5c); this

![Figure 3](image_url)

Figure 3. (Color online) Isotropic/anisotropic nature of AVO\(_3\) shown graphically by Zener’s anisotropy index (\(A_z\)) and the universal \(A^{(U)}\) anisotropy index, where the dash-dotted lines denote the isotropic line.

![Figure 5](image_url)

Figure 5. Structural and electronic properties of the synthesized AVO\(_3\) perovskites. (a) Crystal structure of AVO\(_3\) (Ba\(\rightarrow\)Sr\(\rightarrow\)Ca\(\rightarrow\)Mg). The lowest and highest values of \(\sigma_p\) are observed for MgVO\(_3\) and BaVO\(_3\), respectively. The \(\sigma_p\) values of MgVO\(_3\) and SrVO\(_3\) are comparable to the reported double MgVO\(_3\) and BaVO\(_3\), respectively. The \(\sigma_p\) values of BaVO\(_3\), SrVO\(_3\), and CaVO\(_3\) are comparable to the reported double MgVO\(_3\) and BaVO\(_3\), respectively, and also a negligible energy gap (\(\sim\)0.03 eV) between the valence and conduction bands is observed (Figure 5c).
finding suggests the spin-gapless semiconductor behavior of CaVO$_3$. Hence, the overall behavior of BaVO$_3$ and SrVO$_3$ is half-metallic ferromagnetic, whereas ferromagnetic CaVO$_3$ and MgVO$_3$ behave like spin-gapless and magnetic semiconductors, respectively. It is significant that the valence band of CaVO$_3$ and MgVO$_3$ is very flat just below the $E_F$ with a large dispersion from the R to M point, which may create a van Hove singularity (vHS) at both points. The presence of such a vHS in the band diagram usually denotes the enhanced electronic and electrical carriers as well as electron pairings in the case of superconducting materials. The band gap of ferromagnetic MgVO$_3$ was also reported at about 0.5 eV within the local spin density approximation (LSDA). In this study, the half-metallic nature of AVO$_3$ (A = Ba, Sr, and Ca) is 100% spin-polarized because all the states are present in the spin-up channel, while the spin-down channel has no states. The indirect band of the studied AVO$_3$ compounds may arise owing to the exchange splitting. It is significant that the indirect band gap in the spin-down channel decreases with the cation changing from Ba to Ca as shown in Figure 7. The results are similar to those observed in ref 29.

### 3.3.2. Density of States (DOS).
In order to have a better understanding, the atomic contributions to the band formation of AVO$_3$ compounds, the partial density of states (PDOS), and the total density of states (DOS) have been calculated and are plotted in Figure 6. It is evident from DOS that all the compounds have n-type carriers with a sharp peak for the crossing of electrons at $E_F$. Among them, MgVO$_3$ has a relatively lower class of carriers because of its semiconducting nature. The lower band of AVO$_3$ for both spin-up and spin-down channels is situated at about $-65$ eV, which originated from V 4s states, whereas the lowest band of MgVO$_3$ is located at around $-75$ eV, which stemmed from the Mg 3s state only. The band of BaVO$_3$ originated from the V 3p state for both channels and is situated at around $-39$ eV and shifts to a little

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**Table 4. The Maximum and Minimum Limits of $G$, $Y$, and $\nu$ of AVO$_3$ (A = Ba, Sr, Ca, and Mg)**

| compounds | $G_{\text{max}}$ (GPa) | $G_{\text{min}}$ (GPa) | $E_{\text{max}}$ (GPa) | $E_{\text{min}}$ (GPa) | $\nu_{\text{max}}$ | $\nu_{\text{min}}$ |
|-----------|--------------------------|-------------------------|--------------------------|--------------------------|-------------------|-------------------|
| BaVO$_3$ | 133.62                   | 91.59                   | 320.41                   | 234.41                   | 0.350             | 0.098             |
| SrVO$_3$ | 118.07                   | 110.93                  | 292.60                   | 277.83                   | 0.262             | 0.223             |
| CaVO$_3$ | 118.94                   | 97.68                   | 295.80                   | 250.58                   | 0.334             | 0.214             |
| MgVO$_3$ | 110.13                   | 56.00                   | 278.68                   | 153.52                   | 0.544             | 0.165             |

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Figure 4. (Color online) Directional dependences of the shear modulus, $G$ (upper curves), Young’s modulus, $E$ (middle curves), and Poisson’s ratio, $\nu$ (lower curves), of AVO$_3$ (A = Ba, Sr, Ca, and Mg).
higher energy with the alteration of the cation from Ba to Mg. The bands at about $-25$, $-34$, $-42$, and $-39$ eV of BaVO$_3$, SrVO$_3$, CaVO$_3$, and MgVO$_3$ come from the Ba 6s, Sr 5s, Ca 4s, and Mg 2p states, respectively. The band at around $-18$ eV of BaVO$_3$ and SrVO$_3$ is due to the admixture of dominating O 2s along with minor contributions of V 3p and 3d, Ba 5p and 4d, and Sr 4p and 3d states, whereas the band of CaVO$_3$ is due to the primary contribution of the Ca 3p state along with a little contribution of O 2s. Over these states, around $-16$ to $-11$ eV is demonstrated to be completely p states of Ba and Sr with the minor contributions of s and p states of O for BaVO$_3$ and SrVO$_3$, respectively, whereas in the case of CaVO$_3$ and MgVO$_3$, the band is a major contribution of O 2s with minor contributions of p and d states of V. Finally, the TDOS from $-8$ eV to the Fermi level ($E_F$) has primary contributions from V 3d and O 2p states along with minor contributions of the p state of V and d and s states of Ba and Sr atoms (Figure 6).

To clarify the physical origin of half-metallic ferromagnetism of AVO$_3$ compounds, we also studied the TDOS and PDOS at the $E_F$ for the spin-up channel, which is shown in Figure 7. It is found from Figure 7 that the PDOS value of V 3d and O 2p states decreases by changing cations from Ba to Ca, and the PDOS value of V 3d becomes very small in CaVO$_3$ and MgVO$_3$. The spin-polarized GGA+U ($U = 2.5$ eV for V 3d) calculated electronic band structures of (a) BaVO$_3$, (b) SrVO$_3$, (c) CaVO$_3$, and (d) MgVO$_3$ along the high-symmetry directions in the Brillouin zone.

Figure 5. (Color online) Spin-polarized GGA+U ($U = 2.5$ eV for V 3d) calculated electronic band structures of (a) BaVO$_3$, (b) SrVO$_3$, (c) CaVO$_3$, and (d) MgVO$_3$ along the high-symmetry directions in the Brillouin zone.

Figure 6. (Color online) Total and partial density of states of (a) BaVO$_3$, (b) SrVO$_3$, (c) CaVO$_3$, and (d) MgVO$_3$ with the spin-polarized GGA+U ($U = 2.5$ eV for V 3d) method.

Figure 7. (Color online) (a–d) Total density of states (TDOS) and partial density of states (PDOS) at the Fermi level ($E_F$) of AVO$_3$. (e) Band gap energy ($E_g$) of AVO$_3$ in the spin-down channel.
MgVO$_3$, while the PDOS value of the O 2p state increases in MgVO$_3$. These results indicate that the strong hybridization between V 3d and O 2p is responsible for the half-metallic and semiconductor nature of AVO$_3$, where the V 3d state controls the half-metallic behavior and O 2p dominates the semiconductor nature of the studied compounds.

3.3.3. Electronic Charge Density. The charge density maps of valence electrons are depicted in Figure 8 to comprehend the total electronic charge density distribution of AVO$_3$ compounds. The scale on the right side shows the intensity of electron density. The red color denotes the high density of electrons, whereas the blue color represents the low density of electrons. It is apparent from Figure 8 that the distribution of charge density is essentially spherical around all the atoms of AVO$_3$ compounds. This outcome indicates the ionic nature of AVO$_3$ compounds. The ionic characteristics are also an effect of the metallic characteristics of compounds. As can be seen in Figure 4b, the O–V bonds where the electronic charge transfer from V 3d to O 2p in AVO$_3$ (A = Ba, Ca, and Mg) manifest a half-metallic nature.

3.3.4. Fermi Surface. The Fermi surface topologies of AVO$_3$ compounds are shown in Figure 9. The Fermi surfaces of BaVO$_3$, SrVO$_3$, CaVO$_3$, and other compounds are almost similar. It is seen from the topology that there is a hole-like Fermi surface that looks like a cylindrical cross section with six windows surrounded at the Γ-point. A hole pocket is also present around the X-point connected with the hole-like Fermi surface surrounding the Γ-point. Hence, it is evident that only hole-like Fermi surfaces are present, which reveals the single-band nature of AVO$_3$ (A = Ba, Sr, and Ca) compounds. However, the MgVO$_3$ compound does not show the Fermi surface topology for its semiconducting nature.

3.4. Optical Properties. The material's response to incident electromagnetic radiation can be explained by various optical properties, namely, the dielectric function, the refractive index, conductivity, the absorption coefficient, reflectivity, and the loss function. The real ($\varepsilon_1$) and imaginary ($\varepsilon_2$) parts of the dielectric function of AVO$_3$ compounds are displayed in Figure 10. The damping factor of 0.05 eV and the Drude plasma frequency of 3 eV have been used to study dielectric properties because of the half-metallic nature of AVO$_3$ in the present investigation. In this study, the position of the peak of the real part of the dielectric function is linked to the electron excitation, and the peak is primarily caused by interband transitions. It is apparent from Figure 10 that $\varepsilon_1(\omega)$ shows a peak in the visible region at around 2.30 eV, which is related to the interband transitions. It is well-known that the real part of the dielectric function is linked to the electron excitation, and the peak is primarily caused by interband transitions. However, the MgVO$_3$ compound does not show the Fermi surface topology for its semiconducting nature.
nature of AVO$_3$ in this study. The half-metallic behavior of AVO$_3$ (A = Ba, Sr, and Ca) compounds and semiconductor behavior of MgVO$_3$ are revealed on the basis of their electronic properties. It is important to note that $\varepsilon_2(\omega)$ reaches zero in the ultraviolet region at around 30 eV, which demonstrates that the AVO$_3$ compounds are transparent and optically anisotropic as well. The anisotropic behavior of AVO$_3$ compounds was also found by the elastic properties.

The extinction coefficient ($k$) and the refractive index ($n$) represent the amount of the absorption loss and the phase velocity, respectively, when the electromagnetic wave (as light) passes through the material. The energy-dependent $n$ and $k$ are shown in Figure 11. The calculated values of the static refractive index $n(0)$ of BaVO$_3$, SrVO$_3$, CaVO$_3$, and MgVO$_3$ are found to be 6.14, 5.97, 7.89, and 8.77, respectively, which changes with the applied energy, implying that AVO$_3$ carries photorefractive effects. The relatively high value of the static refractive index suggests that AVO$_3$ can be suited as a potential candidate for application as an ultra-high-density optical storage device upon suitable laser irradiation.

The coefficient of absorption ($\alpha$) provides the measure of energy absorbed by materials and gives information about the solar energy conversion efficiency. From the lower part of Figure 12, the spectra of the absorption coefficient start with a zero value, and the calculated $\alpha$ illustrates a trend similar to $\varepsilon_2(\omega)$. Generally, the peaks with the energy in the infrared range of spectra may arise due to the intraband transition. In contrast, the peaks in the high-energy region of the conductivity and absorption spectra may be from the interband transition. The maximum absorption is found at 19.54, 23.85, 27.47, and 41.02 eV for BaVO$_3$, SrVO$_3$, CaVO$_3$, and MgVO$_3$, respectively. The different high-intensity peaks in the range of 15–30 eV denote various electronic transition rates.

It is worth noting that the real part of the photoconductivity ($\sigma$) spectra of AVO$_3$ (upper part of Figure 12) begins with zero photon energy, albeit MgVO$_3$ shows a small band gap ($E_g$ of $\sim$0.12 eV) in the electronic band structure (Figure 5). Therefore, the conductivity at zero photon energy is a clear indication of the half-metallic nature of BaVO$_3$ and SrVO$_3$ compounds, whereas the conductivity at zero photon energy of MgVO$_3$ denotes the degenerate-like semiconductor material. Hence, the cubic phase of MgVO$_3$ can be a suitable candidate for photovoltaic applications. The maximum values of photoconductivity are observed at 18.62, 23.02, 26.87, and 40.46 eV for BaVO$_3$, SrVO$_3$, CaVO$_3$, and MgVO$_3$, respectively. It is noted from Figure 12 that the photoconductivity spectra vary with the absorption spectra. As a result of absorbing photons, the photoconductivity of AVO$_3$ increases, according to this finding.

The energy-dependent reflectivity ($R$) spectra of AVO$_3$ are depicted in the upper part of Figure 13. The highest reflectivity of AVO$_3$ (A = Ba, Sr, and Ca) is seen in the ultraviolet region, while the highest reflectivity is found in the infrared region in
The peaks in the ultraviolet region give rise to the interband transition, whereas the peaks in the infrared region stem from the intraband transition. The zero frequency value of reflectivity \( R(0) \) is found to be 0.53, 0.52, 0.61, and 0.64 for \( \text{Ba VO}_3 \), \( \text{Sr VO}_3 \), \( \text{Ca VO}_3 \), and \( \text{Mg VO}_3 \), respectively. It is noted that the maximum reflectivity value at zero frequency is seen in the \( \text{Mg VO}_3 \) compound. The high-reflectivity spectra of \( \text{AVO}_3 \) reflect that these materials can be a potential candidate for coating materials to diminish solar heating.

The loss spectra \( (L) \) of \( \text{AVO}_3 \) as a function of energy are shown in the lower part of Figure 13. The energy loss function denotes the loss of energy of a fast electron when it passes through a material.\(^6\) The maximum loss function is connected to the plasma resonance, and the frequency associated with it is defined as the plasma frequency, \( \omega_p \). The maximum loss function of \( \text{Ba VO}_3 \), \( \text{Sr VO}_3 \), \( \text{Ca VO}_3 \), and \( \text{Mg VO}_3 \) is found at 25.99, 27.91, 29.45, and 23.95 eV, respectively, which implies the plasma frequency of the respective compound. The results are similar to those observed in ATiO\(_3\) (\( A = \text{Ba}, \text{Sr}, \text{Ca}, \text{and Pb} \)).\(^23\) The \( \text{AVO}_3 \) materials become transparent when the incident light frequency is higher than the plasma frequency. In addition, the loss function peak related to \( \omega_p \) corresponds to the zero-crossing of \( \varepsilon_2 \) with small \( \varepsilon_1 \) (Figure 10), and it correlates with the edge in the reflectivity spectrum in which a sudden reduction of the maximum reflectivity spectrum occurs (Figure 13). It is worth seeing that the value of \( \omega_p \) increased by varying cations from \( \text{Ba} \) to \( \text{Ca} \), while the value of \( \omega_p \) significantly decreased in \( \text{Mg VO}_3 \). The significant decrease in \( \omega_p \) may be due to the semiconductor nature and/or the larger effective mass of free electrons of the \( \text{Mg VO}_3 \) compound.

### 3.5. Population Analysis

The analysis of the Mulliken atomic population provides interesting information regarding the chemical bonding nature of solids.\(^6\) The calculated Mulliken atomic populations of \( \text{AVO}_3 \) are listed in Table 4. As can be seen from Table 5, \( A = \text{Ba, Sr, Ca, and Mg} \) and V atoms carry positive charges, while O atoms carry negative charges, implying that the sharing of charges occurs from \( A \) and \( V \) to \( O \) atoms. We also studied the bond overlap population (\( P^o \)) in order to have a better understanding of the bonding nature of the \( \text{AVO}_3 \) compounds. The zero value of the bond overlap population expresses a perfectly ionic bond, whereas the deviation from zero reflects the increasing levels of covalency.\(^6\) The deviation of \( P^o \) from zero is clearly seen in Table 6, which reveals the covalent nature of these compounds. It is noted in Table 6 that the \( V-O \) bond in \( \text{Ba VO}_3 \) is more covalent than the other compounds. It is also found that the value of \( P^o \) for the \( V-O \) bond is positive, whereas the value of \( P^o \) is negative for the \( A-V \) (\( A = \text{Ba, Sr, Ca, and Mg} \)) and \( O-O \) bonds. The positive and negative magnitudes of \( P^o \) denote the direct and indirect bonds of atoms involved in \( \text{AVO}_3 \) compounds, respectively. The calculated values of spin (Table 5) indicate that the \( V \) atom is mainly accountable for the magnetic properties of \( \text{AVO}_3 \) compounds. We have also calculated the net magnetic moments of \( \text{AVO}_3 \) and summarized them in Table 5. The detailed magnetic properties of \( \text{AVO}_3 \) compounds were studied by researchers earlier.\(^2\) The net magnetic moments of \( \text{AVO}_3 \) under this inspection somewhat differ from the value reported in ref 29. However, the value of the net magnetic moment of \( \text{Mg VO}_3 \) is in good agreement with the value found in ref 66.

### 3.6. Thermodynamic Properties

To understand the behavior of \( \text{AVO}_3 \) under high temperatures and pressures, we have investigated the various thermodynamic properties such as melting temperature, \( T_m \), Debye temperature, \( \theta_D \), and minimum thermal conductivity, \( K_{\text{min}} \). \( \theta_D \) is an essential parameter of solids to rationalize some interesting physical processes related to phonons, specific heat, melting point, thermal conductivity, etc.\(^6\) The value of \( \theta_D \) can be estimated using the average sound velocity using the following equation:\(^6\)

\[
\theta_D = \frac{h}{k_B} \left[ \frac{3m(N_i\rho)}{4\pi M} \right]^{1/3} v_m
\]  

(4)
Table 7. The Calculated Density, \( (\rho) \), Debye Temperature, \( (\theta_D) \), Longitudinal, Transverse, and Average Sound Velocities \( (v_L, v_T, \text{and} \ v_m) \), Minimum Thermal Conductivity \( (K_{\text{min}}) \), and Melting Temperature \( (T_m) \) of AVO3 Compounds

| Compounds | \( \rho \) (g/cm\(^3\)) | \( v_L \) (km/s) | \( v_T \) (km/s) | \( v_m \) (km/s) | \( \theta_D \) (K) | \( T_m \) (K) | \( K_{\text{min}} \) (W m\(^{-1}\) K\(^{-1}\)) | \( \gamma \) |
|-----------|----------------|----------------|----------------|----------------|--------------------|----------------|---------------------------------|-------|
| BaVO\(_3\) | 6.479 | 7140 | 4213 | 4668 | 605 | 1704 | 1.22 | 1.42 |
| SrVO\(_3\) | 5.514 | 7856 | 4567 | 5067 | 673 | 1861 | 1.39 | 1.47 |
| CaVO\(_3\) | 4.295 | 8810 | 4968 | 5526 | 745 | 1933 | 1.57 | 1.59 |
| MgVO\(_3\) | 3.909 | 8712 | 4351 | 4881 | 664 | 1906 | 1.41 | 2.01 |

where \( k_B \) and \( h \) denote the Boltzmann and Planck constants, respectively. \( \rho \) is the density, and \( N_A \) is Avogadro’s number. \( V_v \) and \( M \) are the volume of a unit cell, the number of atoms within a unit cell, and molecular weight, respectively. \( v_m \) implies the average sound velocity in the crystal, which is calculated using the following equation:

\[
v_m = \left[ \frac{1}{3} \left( \frac{2}{v_L} + \frac{1}{v_T} \right) \right]^{-1/3}
\]

Here, \( v_L \) and \( v_T \) denote the transverse and longitudinal sound velocities, respectively. The following expressions can be used to calculate \( v_L \) and \( v_T \) using the shear modulus, \( G \), and the bulk modulus, \( B \):

\[
v_L = \frac{B + \frac{4}{3}G}{\rho} \quad \text{and} \quad v_T = \left[ \frac{G}{\rho} \right]^{1/2}
\]

The melting temperature, \( T_m \), of the AVO3 compounds has also been calculated via the following empirical formula using elastic constants, \( C_{11} \):

\[
T_m = 354 + \frac{4.5(2C_{11} + C_{33})}{3}
\]

In a cubic structure, the axial lengths are equal; thus, \( C_{11} = C_{22} = C_{33} \). The Poisson’s ratio, \( \nu \), is the ratio of lateral strain to axial strain due to a uniaxial stress. In a cubic lattice, the Poisson ratio is related to the elastic constants as:

\[
\nu = \frac{C_{12}}{C_{11}}
\]

where \( C_{12} \) is the shear modulus.

The Grüneisen parameter \( (\gamma) \) provides information regarding anharmonic effects, i.e., the temperature-dependent phonon dampings and frequencies as well as the thermal expansion effects. The Grüneisen parameter is explained by the following:

\[
\gamma(\omega_n) = \frac{d \ln(\omega_n)}{d \ln(\Phi)}
\]

where \( \omega_n \) and \( \Phi \) are the angular frequency and the packing fraction of crystals, respectively. The value of \( \gamma \) can be estimated by a simple expression related to Poisson’s ratio\(^{71}\) as follows:

\[
\gamma = \frac{3(1 + \nu)}{2(2 - 3\nu)}
\]

The calculated values of Debye temperature, \( \theta_D \), with different sound velocities (\( v_L \), \( v_T \), and \( v_m \)), melting temperature, \( T_m \), the Grüneisen parameter, \( \gamma \), and minimum thermal conductivity, \( K_{\text{min}} \), of AVO3 under this study are listed in Table 7. In general, a higher Debye temperature is associated with a higher phonon thermal conductivity and vice-versa. The relatively high values of \( \theta_D \) and \( K_{\text{min}} \) of AVO3 imply a high thermal conductivity, and they might not be suitable for use as a thermal barrier coating (TBC) material.

4. CONCLUSIONS

In this study, we have investigated various physical properties of the cubic phase of AVO3 (A = Ba, Sr, Ca, and Mg) compounds. The calculated lattice parameters show very fair agreement with the available experimental data, implying the reliability of these computational calculations. The mechanical stability of AVO3 is confirmed by the Born stability criteria. The Poisson’s and Pugh’s ratios reveal the ductile behavior of CaVO3 and MgVO3, whereas a brittle nature is exhibited by BaVO3 and SrVO3. The analysis of various anisotropy indices shows that BaVO3, CaVO3, and MgVO3 are anisotropic, whereas SrVO3 exhibits insignificant anisotropy. The intermediate values of Peierls stress were found in AVO3. The AVO3 (A = Ba, Sr) compounds exhibit half-metallic character, whereas CaVO3 and MgVO3 show spin-glass and magnetic semiconductor-like behavior along with n-type carriers, respectively. The half-metallic nature of AVO3 stems mainly from p–d hybridization between O and V atoms. The single-band nature and the presence of hole-like Fermi surfaces are seen. The bonding properties reveal that AVO3 possesses intratomic bonding with a mixture of covalent, ionic, and metallic interactions. Numerous thermodynamic behaviors of AVO3 are calculated using relevant equations and analyzed properly based on the obtained results. The study of optical properties, especially the refractive index of these compounds, indicates that all the materials could be used as promising high-density optical data storage.

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