

Electronic structure, structural phase stability, optical and thermoelectric properties of $\text{Sr}_2\text{AlM}'\text{O}_6$ ($\text{M}' = \text{Nb}$ and Ta) from first principle calculations

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Abstract

First principle calculations are performed to investigate the electronic structure, structural phase stability, optical properties and thermoelectric properties of double perovskite oxide semiconductors namely $\text{Sr}_2\text{AlM}'\text{O}_6$ ($\text{M}' = \text{Nb}$ and Ta) in the cubic symmetry using WIEN2k. In order to study the ground state properties of these compounds, the total energies are calculated as a function of reduced volumes and fitted with Brich Murnaghan equation. The estimated ground state parameters are comparable with the available experimental data. Calculations of electronic band structure on these compounds have been carried out using generalized gradient approximations and modified Becke-Johanson potential (TB-mBJ). The calculated band gap for $\text{Sr}_2\text{AlNbO}_6$ and $\text{Sr}_2\text{AlTaO}_6$ with GGA and TB-mBJ reveal that these compounds exhibit semiconducting behavior with a direct band gap. To explore the optical transitions in these compounds, the real and imaginary parts of the dielectric function, refractive index, extinction coefficient, reflectivity, optical absorption coefficient, real part of optical conductivity and the energy-loss function are calculated at ambient conditions and analyzed both with GGA and TB-mBJ potentials. Investigations of the thermoelectric properties of these compounds have been carried out by the calculations of transport coefficients based on Boltzmann transport theory in order to analyze the variation of Seebeck's coefficient at different temperatures for various carrier concentrations based on the electronic structure near the valence band maxima.

Keywords: Ab-Initio calculations; Double perovskites; Electronic structure; Optical properties; Thermoelectric properties

1. Introduction

Double Perovskite structured oxides compounds with general formula $\text{A}_2\text{BB}'\text{O}_6$ have been widely investigated in the past few decades due to their diversity in their crystal structure and variety of properties such as high temperature superconductivity and colossal magneto-resistance [1] and [2] which are of great importance for scientific and technological applications. These perovskite oxides have become more and more important and are a key material in developing oxide based electronic devices since they show some important properties such as high dielectric constant, ferroelectric polarization, catalysis and magnetic media [3] and [4]. Investigation of double perovskite type compounds in the areas of fuel cells is very essential since these materials are a promising anode material for the solid state fuel cells which are anticipated for operation at moderate temperature [5] and [6]. Semiconducting oxide perovskites are of technological importance since these oxides are used to develop dielectric resonators and filters. These dielectric resonators and filters are used in microwave

signal devices like mobile phones and other wireless devices [7]. Many microwave dielectric ceramics adopt perovskite structure with low dielectric loss and high dielectric constant, hence these materials are employed enormously in microwave integrated circuits [8].

Enormous amount of work has been done experimentally on these semiconducting oxides with perovskite structure in ideal, double and complex structures. Mishra et al. [9] using angle dispersive X-ray diffraction and Raman scattering, studied the structure evolution of double perovskite Sr_2MgWO_6 under high pressure. This compound is found to be structurally stable with tetragonal structure (space group $I4/m$) up to the highest pressure of about 40 GPa. These experimental reports were also confirmed with the use of first principles structural relaxation calculations. Bouchaib Manoun et al. [10], reported the high temperature (up to 500°C) Raman spectroscopy phase transitions in Sr_2MWO_6 ($\text{M} = \text{Zn}, \text{Co}$) double perovskite oxides. It is observed that a first order phase transition from monoclinic ($P21/n$) to tetragonal ($I4/m$) structure occurs at a temperature of 80°C for Sr_2ZnWO_6 , whereas Sr_2CoWO_6 undergoes phase transition from tetragonal ($I4/m$) to cubic ($Fm-3m$) at a temperature of about 480°C . Yan Qian et al. [11] studied the effect of high pressure on the electronic and magnetic properties of $\text{Sr}_2\text{FeMoO}_6$ and reported a transition from a ferromagnetic half-metallic state to nonmagnetic semiconductor state at a pressure of about 33–36 GPa by replacing Ba with Sr using synchrotron X-ray and neutron powder diffraction methods.

Alo Dutta et al. [12] synthesized $\text{Sr}_2\text{AlNbO}_6$ by a solid state reaction and studied the dielectric property. The dielectric properties of this compound show significant frequency dispersion. The dielectric relaxation of $\text{Sr}_2\text{AlNbO}_6$ is studied by Cole–Cole model. Recently using first principles calculations Li et al. [13] reported that $\text{Sr}_2\text{AlTaO}_6$ exhibit induced ferromagnetism due to vacancy in Al and Ta. The induced magnetism is different for Al and Ta vacancy. Their study reveals that $\text{Sr}_2\text{AlTaO}_6$ with O vacancy is nonmagnetic but energetically more favorable than that of other vacancies.

It is well known that metals have very good electrical conductivity ($\sim 10^6 \Omega^{-1} \text{cm}^{-1}$). However, their very low Seebeck coefficient ($\sim 5 \mu\text{VK}^{-1}$) and large thermal conductivity do not make them the most desirable materials for thermoelectric applications. Semiconductors with large band gap are having large Seebeck coefficient ($\sim 1000 \mu\text{VK}^{-1}$) with very low electrical conductivity ($\sim 10^{-12} \Omega^{-1} \text{cm}^{-1}$) results in a small value of $S^2\sigma$. In thermoelectric materials research, favorable oxide thermoelectric materials have been discovered, which include CaMnO_3 -based perovskites, Al-doped ZnO, layered cobalt oxides represented by NaCo_2O_4 and $\text{Ca}_3\text{Co}_4\text{O}_9$, and SrTiO_3 -related phases. It is well known that TMF (thermo electromotive force) generated by metals is generally less than $50 \mu\text{V/K}$, however semiconductors can generate the TMF of several hundreds of $\mu\text{V/K}$.

From the above reports, it is interesting to note that several experimental studies have been done on these Strontium based double perovskites. However only few theoretical studies are reported particularly on the optical and thermoelectric properties of Strontium based compounds namely $\text{Sr}_2\text{AlNbO}_6$ and $\text{Sr}_2\text{AlTaO}_6$. It is well known that Niobium and Tantalum based double perovskites are of great importance since these materials are used extensively in many technological applications such as interference filters, optical fibers, solar energy conversion, reflecting coatings, pigments and photo catalysts. Hence accurate knowledge of their optical

constants is essential. First principles calculations offer one of the most powerful tools for carrying out theoretical studies of these properties.

2. Method of calculations

In this work, the structural phase stability and electronic structure calculation of $\text{Sr}_2\text{AlM}'\text{O}_6$ ($M' = \text{Nb}$ and Ta) compounds were carried out using the full potential LAPW method implemented in WIEN2K [14] within the generalized gradient approximation (GGA) to the exchange-correlation potential according to the Perdew-Burke-Ernzerhof parameterization [15]. The muffin tin radii for Sr, Al, Nb, Ta and O are 2.50, 1.80, 1.98, 1.97 and 1.75 a.u. respectively. The Brillouin zone sampling was performed according to the Monkhorst-Pack scheme [16]. For k-space integration 5000 k points in the entire Brillouin zone were used. The number of plane waves in a Fourier expansion of potential in the interstitial region was restricted to $R_{\text{MT}} \times k_{\text{max}} = 7$. For the total energy calculations the energy convergence criterion was set to 10^{-6} Ry.

The transport calculations in the present study are carried out using the code Boltztrap[17]. This calculation is based on the semi classical treatment given by the solution of Boltzmann equation by embedding certain approximations like relaxation time approximation and rigid body approximation. Considering these approximations, the Seebeck coefficient $S(T, \rho)$ which depends on temperature and doping is given by [18].

where f is the Fermi function, μ is the chemical potential and $\sigma(E)$ is the transport function by

where $N(E)$ is the density of states (DOS), $\gamma(E)$ is the band velocity and $\tau(E)$ is the scattering time. Under the constant scattering time approximation $\tau(E)$ is independent of energy [17] and [18]. In order to assess thermoelectric power factor $S^2\sigma$, the term $\sigma(T)$ is required and is given by

3. Crystal structure

An ideal single perovskites have the same crystal structure similar to CaTiO_3 a natural mineral with general formula AMX_3 , where A is a cation normally with large radius and low charge, such as an alkali or alkaline earth metal. The M cations are usually transition metal ions having smaller radius with more electro negativity. Generally the X anion is replaced by oxygen, fluorine or nitrogen. In the ideal perovskite structure AMO_3 , if site of the M cation is substituted partially in a 1:1 manner by M' cation a crystal structure of an ideal double perovskite is obtained with expanded unit cell and the cell parameters of these double perovskite are approximately twice those of an ideal perovskite. Thus, the crystal structure of an ideal double perovskite with general formula $\text{A}_2\text{MM}'\text{O}_6$ can be described as a frame work of alternating MO_6 and $\text{M}'\text{O}_6$ octahedra in three dimension, with A-cations occupying the interstitial spaces between the octahedra. At ambient conditions $\text{Sr}_2\text{AlM}'\text{O}_6$ ($M' = \text{Nb}$ and Ta) crystallizes in a cubic structure (space group Fm-3m). The atomic positions of Sr atom is at (8c) (0.25, 0.25, 0.25), Al atom is at (4a) (0,0,0), M' atom is at (4b) (0.5, 0.0, 0.0) and for O is at (24e) (u, 0, 0), where 'u' is the internal parameter of the oxygen atom [23].

4. Structural phase stability

In the present calculation a complete structural optimization was performed for both the compounds. The optimized lattice parameter and the atomic positions show that these compounds adopt the cubic symmetry with space group Fm-3m. To verify the above result the tolerance factor (T_f) for these compounds is calculated using the formula

where R_A denotes the ionic radius of Sr ion and R_o denotes the ionic radius of O ions. R_B denotes the average ionic radius of the ions at M' sites. The tolerance factor is an important parameter for a perovskite structure which provides direct information about the structural stability. The perovskite structure is stable within the tolerance range of $0.78 < T_f < 1.05$. For calculation of tolerance factor for Sr_2AlNbO_6 and Sr_2AlTaO_6 the ionic radius of Sr, Al, Nb, Ta and O ions are taken as 1.12, 0.535, 0.64, 0.64, and 1.4 Å, respectively. The calculated tolerance factor is found to be 0.90 which supports that the cubic structure is stable.

Owing to the cubic symmetry, the equilibrium lattice constant of these perovskite is determined by the minimization of the total energy of the system with respect to the volume of the unit cell as similar to our earlier works [19], [20] and [21]. The calculated total energies are fitted with Birch–Murnaghan equation of state [22] to estimate the equilibrium lattice constant. The double perovskite compounds are characterized by the internal parameter ‘u’ which specify the position of ‘O’ anion in the unit cell. In the present calculation, the value of the internal parameters ‘u’ has been optimized at equilibrium volume and the optimized parameters are also tabulated. The total energy as a function of the volume for these compounds is shown in Fig. 1 and Fig. 2. The estimated lattice parameters are presented in Table 1, together with the available experimental data [23].

Compound	ao(Å)	u	B_0 (GPa)	B'
Sr_2AlNbO_6	7.7832	0.2448	172.0	5.78
	7.7858 ^a	0.2450 ^a		
Sr_2AlTaO_6	7.7839	0.2460	170.4	5.80
	7.7866 ^a	0.2461 ^a		

5. Results and discussions

5.1. Electronic band structure

The band structure of the double perovskite $Sr_2AlM'O_6$ ($M' = Nb$ and Ta) at zero pressure along highly symmetrical points in the Brillouin zone show that the bands just fall below the Fermi level (E_F) are derived

from O-2p orbitals. The overall band profiles of two compounds exhibit the same nature of band profiles. The calculated band structures clearly show that valence band maximum and conduction band minimum falls at Γ point. Therefore, the band gap of these materials is the $\Gamma - \Gamma$ direct gap semiconductor with a band gap of 3.03 eV and 3.75 eV for $\text{Sr}_2\text{AlNbO}_6$ and $\text{Sr}_2\text{AlTaO}_6$ respectively. It is well known that in direct gap materials excess of energy is released as photon when an electron in the conduction band annihilates a hole in the valence band. This emission of photon energy is faster in direct band gap materials than in the indirect band gap materials. Because of this reason most of the wide band gap semiconductors are used in designing of optoelectronic devices. Since the compounds $\text{Sr}_2\text{AlNbO}_6$ and $\text{Sr}_2\text{AlTaO}_6$ are wide band gap materials they are very useful in designing light emitting diodes and laser diodes working in the visible and ultra-violet region. The calculated band gap of $\text{Sr}_2\text{AlNbO}_6$ and $\text{Sr}_2\text{AlTaO}_6$ is lower than that of experimental value [24]. It is well known that the band gap calculated using local density approximation (LDA) and GGA strongly underestimate experimental band gap [25]. In order to get a good estimate of the energy band gap values, the modified Becke-Johanson potential (TB-mBJ) as proposed recently by Tran and Blaha [26] is also employed. This potential can be used to produce accurate gaps for a wide range of different materials [27], [28], [29], [30], [31], [32] and [33]. The calculated band gap using TB-mBJ for $\text{Sr}_2\text{AlNbO}_6$ is exactly matches with experimental value of 3.8 eV. However, the calculated band gap for $\text{Sr}_2\text{AlTaO}_6$ using TB-mBJ is 5.03 eV, which is slightly more than the experimental energy gap. The calculated energy gaps for these compounds with GGA and TB-mBJ are tabulated in Table 2, along with the available experimental data.

Table 2.

The calculated and experimental band gaps for $\text{Sr}_2\text{AlM}'\text{O}_6$ ($M' = \text{Nb}$ and Ta) compounds.

Compound	GGA (eV)	TB-mBJ (eV)	Experiment (eV)
$\text{Sr}_2\text{AlNbO}_6$	3.03	3.80	3.80 ^a
$\text{Sr}_2\text{AlTaO}_6$	3.75	5.03	4.60 ^a

The calculated band structure of $\text{Sr}_2\text{AlNbO}_6$ and $\text{Sr}_2\text{AlTaO}_6$ with GGA and TB-mBJ are shown in Fig. 3(a-d).

To further explain the nature of the electronic band structure the total DOS of $\text{Sr}_2\text{AlNbO}_6$ and $\text{Sr}_2\text{AlTaO}_6$ are calculated and are shown in Fig. 4(a-d) with GGA and Tb-mBJ potentials. The GGA density of states profile of these compounds clearly depicts that O-p states electrons contribution is more in the valence band region from 0 to -4.5 eV and hybridize with Al-p states. In the conduction band the transition metals Nb and Ta mainly contribute for the bands in the energy range from 3 to 10 eV. The covalency nature between Nb-4d to O-2p in $\text{Sr}_2\text{AlNbO}_6$ and Ta-5d to O-2p covalency in $\text{Sr}_2\text{AlTaO}_6$ is because of the fact that at the valence band maximum the Nb-4d contribution and Ta-5d contribution are zero but it rises with increasing energy. On the other hand at the conduction band minimum the O-2p contribution rises from zero with increase of energy. The density states profiles of these compounds with TB-mBJ are similar with an energy shift of 0.77 eV for $\text{Sr}_2\text{AlNbO}_6$ and 1.28 eV for $\text{Sr}_2\text{AlTaO}_6$ when compared with GGA.

5.2. Optical properties

The optical properties of matter can be described by the electronic dielectric function $\epsilon(\omega)$. Generally, there are two contributions for $\epsilon(\omega)$, namely intraband and interband transitions. The latter contributions are crucial only for metals [34]. The interband transitions can be further divided into direct and indirect transitions. Here the indirect interband transitions are ignored since it involves scattering of phonon and is expressed to give only a small contribution to $\epsilon(\omega)$. The dielectric function of an anisotropic material is a complex symmetric second-order tensor which describes the linear response of an electronic system to an applied external electric field. It can be expressed as $\epsilon(\omega) = \epsilon'(\omega) + i\epsilon''(\omega)$, where $\epsilon'(\omega)$ and $\epsilon''(\omega)$ are the real and imaginary components of the dielectric function, respectively. The imaginary part of the frequency dependent dielectric function, is given by [35]:

The integral is over the first Brillouin zone. The momentum dipole elements: $M_{cv}(\mathbf{k}) = \langle u_{cv} | \delta \cdot \nabla | u_{vk} \rangle$, where δ is the potential vector defining the electric field, are matrix elements for direct transitions between valence- $u_{vk}(\mathbf{r})$ and conduction-band $u_{ck}(\mathbf{r})$ states, and the energy $\hbar\omega_{cv}(\mathbf{k}) = E_{ck} - E_{vk}$ is the corresponding transition energy. The real part of the dielectric function $\epsilon'(\omega)$ can be derived from the imaginary part using the Kramers–Kronig relations,

where, P implies the principal value of the integral. The knowledge of both the real and imaginary parts of the dielectric function allows the calculation of important optical functions such as, refractive index $n(\omega)$, extinction coefficient $k(\omega)$, reflectivity $R(\omega)$, optical absorption coefficient $I(\omega)$, real part of optical conductivity $\text{Re}[\sigma(\omega)]$ and the energy-loss function $L(\omega)$ using the following

These compounds $\text{Sr}_2\text{AlNbO}_6$ and $\text{Sr}_2\text{AlTaO}_6$ have cubic symmetry. For cubic symmetry, the principal tensor component ϵ_{xx} , ϵ_{yy} and ϵ_{zz} will be equal. Hence only one component of the dielectric function has to be calculated i.e, $\epsilon_{xx} = \epsilon_{yy} = \epsilon_{zz}$. The variations in the real and imaginary (absorption) parts of the electronic dielectric function (ϵ_0) for $\text{Sr}_2\text{AlNbO}_6$ and $\text{Sr}_2\text{AlTaO}_6$ with GGA and TB-mBJ are shown in Fig. 5a and b.

The analysis of the $\epsilon''(\omega)$ curve with GGA shows that the first optical critical point of the dielectric function occurs at 3.03 eV for $\text{Sr}_2\text{AlNbO}_6$ and at 3.75 eV for $\text{Sr}_2\text{AlTaO}_6$, whereas with TB-mBJ potential the first optical critical point of the dielectric function occurs at 3.8 eV for $\text{Sr}_2\text{AlNbO}_6$ and at 5.03 eV for $\text{Sr}_2\text{AlTaO}_6$. This point is $\Gamma_v - \Gamma_c$ splitting, which gives the threshold of direct optical transitions between the highest valence band maximum and the lowest conduction band minimum. This is known as the fundamental absorption edge.

Beyond this point the curve increases rapidly. This is due to the fact that the number of points contributing towards $\epsilon''(\omega)$ increases abruptly. The main peak of $\epsilon''(\omega)$ spectrum for $\text{Sr}_2\text{AlNbO}_6$ and $\text{Sr}_2\text{AlTaO}_6$ with GGA is situated at 4.4 eV and 5.3 eV respectively. For the real part ($\epsilon'(\omega)$) spectrum, the main peak, with a magnitude of 8.5 for $\text{Sr}_2\text{AlNbO}_6$, is situated at 4.1 eV and for $\text{Sr}_2\text{AlTaO}_6$ the main peak with a magnitude of 8.2, is situated at 4.9 eV. The main peak of the real part and imaginary spectrum with TB-mBJ occurs with a shift towards the higher energies as compared to GGA.

The static dielectric constant $\epsilon'(0)$ is the most important quantity which is obtained as the zero frequency limit of the real part of the frequency-dependent dielectric function. The calculated values of static dielectric function $\epsilon'(0)$ for both the compounds with GGA and TB-mBJ are given in Table 3. This important quantity is related to the band gap and shows that a smaller energy gap yields a larger value of the static dielectric constant $\epsilon'(0)$. This could be explained on the basis of the Penn model [36]. The Penn model is based on the expression $\epsilon_0 = 1 + (\hbar\omega_p/E_g)^2$. It is noted from the expression that the static dielectric constant $\epsilon'(0)$ of a compound is inversely proportional to E_g . Hence, smaller E_g yields larger (ϵ_0).

Compound	XC	$\epsilon'(0)$ (eV)	$n(0)$	$k(0)$	$R(0)$	$I(0)$ (eV)	$\sigma(0)$ ($\Omega \text{ cm}^{-1}$)	$L(0)$ (eV)
$\text{Sr}_2\text{AlNbO}_6$	GGA	4.12	2.03	1.69	0.12	3.03	7214.70	5.84
	TB-mBJ	3.17	1.78	1.55	0.08	3.80	7876.09	6.38
$\text{Sr}_2\text{AlTaO}_6$	GGA	3.72	1.90	1.60	0.10	3.75	6240.60	6.13
	TB-mBJ	2.73	1.65	1.39	0.06	5.03	6604.45	7.38

The refractive index $n(\omega)$ of $\text{Sr}_2\text{AlNbO}_6$ and $\text{Sr}_2\text{AlTaO}_6$ calculated with both potentials as obtained from expression (3) are shown in Fig. 6. The maximum refractive index $n(\omega)$ for $\text{Sr}_2\text{AlNbO}_6$ and $\text{Sr}_2\text{AlTaO}_6$ is obtained at energy of 4.2 eV and 4.9 eV respectively for GGA, whereas the maximum refractive index with TB-mBJ is obtained at 4.9 eV and 6.2 eV for $\text{Sr}_2\text{AlNbO}_6$ and $\text{Sr}_2\text{AlTaO}_6$ respectively indicating the shift towards the higher energies. The maximum refractive index is established at the first transition of an electron from valence band to conduction band. This type of transition is called direct electron transition. At higher energies the refractive index decreases for the reason that there is no possibility for direct de-excitation of electron and consequently there is dissipation of energy. It is well known that semiconductors having lower refractive indices have wider band gap which dictate an inverse relation between the zero frequency limit of the refractive index and band gap of semiconductor.

It is clear from Fig. 6 that the refractive index of both the compounds and higher energies is lesser than unity which is a clear indication that the two compounds are no longer active as a transparent material. The refractive index is the complex variable given as $N(\omega) = n(\omega) + jk(\omega)$, where $k(\omega)$ is called the extinction coefficient.

The variation of extinction coefficient with photon energy is shown in Fig. 7. The extinction coefficient of $\text{Sr}_2\text{AlNbO}_6$ increases with energy in the transparency region and reaches its maximum value at about 4.6 eV whereas for $\text{Sr}_2\text{AlTaO}_6$ the maximum value is at energy of 5.4 eV. The larger values of extinction coefficient in these compounds reveal that these compounds have the affinity to absorb more light.

The important optical constants like reflectivity $R(\omega)$, optical absorption coefficient $I(\omega)$, real part of optical conductivity $\text{Re}[\sigma(\omega)]$ and the energy-loss function $L(\omega)$ are calculated using expressions (7)–(11) and are shown in Fig. 8(a–d) with GGA and TB-mBJ. From Fig. 8(a) the reflectivity profile of $\text{Sr}_2\text{AlNbO}_6$ clearly shows the location of four peaks at energy of 4.55, 8.28, 10.46, and 12.72 eV. However for $\text{Sr}_2\text{AlTaO}_6$ four peaks are observed at energy of 5.40, 9.37, 11.60, and 12.30 eV. The low value of reflectivity in these compounds makes sure its potential applications in the area of transparent coatings in the visible and deep UV region. The calculated linear absorption and the real part of optical conductivity from expressions (5) and (6) for $\text{Sr}_2\text{AlM}'\text{O}_6$ ($M' = \text{Nb}$ and Ta) are shown in Fig. 8(b) and (c). For $\text{Sr}_2\text{AlNbO}_6$ the absorption spectrum has four peaks located at energy of 4.63, 8.58, 9.26, and 10.13 eV. For $\text{Sr}_2\text{AlTaO}_6$ four peaks are located at energy of 5.40, 9.37, 11.60, and 12.30 eV.

It is clear that for both the compounds the peaks obtained in the absorption spectrum matches with the peaks of imaginary part of the dielectric function $\varepsilon''(\omega)$ which indicates that the origin of absorption is due to the imaginary part of the dielectric function. From the absorption spectrum it is clear that at the lower energies the absorption coefficient decreases rapidly which is a well known behavior for semiconductors and insulators. The profile of real part of optical conductivity shown in Fig. 8(c) shows similar peaks as obtained in the absorption spectrum and the maximum optical conductivity occurs at energy of 9.27 eV for $\text{Sr}_2\text{AlNbO}_6$ and 11.20 eV for $\text{Sr}_2\text{AlTaO}_6$. The absorption spectral peaks in TB-mBJ are shifted about 0.77 eV for $\text{Sr}_2\text{AlNbO}_6$ and 1.28 eV for $\text{Sr}_2\text{AlTaO}_6$ towards the higher energies.

Fast moving electrons passing through a material can be described by an important optical parameter known as electron loss function $L(\omega)$. The energy at which this function becomes maximum is called Plasmon energy whose position corresponds to the zero crossing point of the real part of the dielectric constant $\varepsilon'(\omega)$. The electron loss functions of $\text{Sr}_2\text{AlNbO}_6$ and $\text{Sr}_2\text{AlTaO}_6$ are calculated and are presented in Fig. 8(d). From the figure the highest energy loss function with GGA occurs at 5.84 eV and 6.13 eV for $\text{Sr}_2\text{AlNbO}_6$ and $\text{Sr}_2\text{AlTaO}_6$ respectively. For TB-mBJ potential the highest energy loss function occurs at 6.13 eV and 7.38 eV for $\text{Sr}_2\text{AlNbO}_6$ and $\text{Sr}_2\text{AlTaO}_6$ respectively. The sharp peak obtained in the electron loss spectrum corresponds to the abrupt reduction of reflectivity spectrum of these compounds. The calculated value of refractive $n(\omega)$, extinction coefficient $k(\omega)$, reflectivity $R(\omega)$, optical absorption coefficient $I(\omega)$, real part of optical conductivity $\text{Re}[\sigma(\omega)]$ and the energy-loss function $L(\omega)$ for both the compounds with GGA and TB-mBJ potentials are tabulated in Table 3.

5.3. Thermoelectric properties of $\text{Sr}_2\text{AlM}'\text{O}_6$ ($M' = \text{Nb}$ and Ta)

In the present scenario it is very clear that conventional energy resource is fast degrading. An investigation for alternative energy resources coupled with the anxiety to reduce the environmental impact is essential, since the

demand of energy is fast increasing. The new alternative way of generation of electricity is the Seebeck effect because this effect is one of the most environmental friendly methods of generating electricity. The materials which generate this nature of electricity are called as thermoelectric materials.

The major challenge of this effect is the generation of very low efficiency thermoelectricity when compared with the conventional ways of producing electricity. The efficiency of thermoelectricity generated by this method is specified by a dimensionless quantity called the figure of merit (ZT). Generally the ZT is given by $ZT = S^2\sigma T/k$, where S is the Seebeck coefficient, also known as thermo power, σ is the electrical conductivity, T is the absolute temperature and k is the total thermal conductivity of the material. It is well known that the thermal conductivity of a material is the sum of lattice thermal conductivity k_l and electronic thermal conductivity k_e .

From the expression of figure of merit it is very clear that increasing the efficiency of thermoelectricity can be achieved by two possible routes. (i) To attain larger values of S and σ and smaller value of k_e of thermoelectric materials. This might be possible by tuning the electronic structure of these materials thereby increasing the thermoelectric performance. (ii) Reducing the thermal conductivity due to lattice contributions k_l which in turn reduces the total conductivity k of the material. The above discussion clearly indicates that the thermoelectric behavior of a material is based on the electronic structure, hence in the present work it is mainly focused on the thermoelectric behavior of $Sr_2AlM'O_6$ compounds by looking into its electronic structure from the first principles calculations.

A material being thermoelectric is mainly based on the electronic structure particularly near the valence band maximum (VBM). The thermoelectric performance of a material is based on figure of merit and it is directly proportional to Seebeck coefficient and electrical conductivity σ . For improving the Seebeck coefficient the key factor is the presence of flat bands at the valence band maximum which corresponds to a large effective mass. On the other hand the electrical conductivity σ is increased by the presence of more dispersive band at the valence band maximum which corresponds to lighter effective mass implying higher mobility [37].

The band structure of $Sr_2AlM'O_6$ compounds depicted in Fig. 3(a–d), show similar nature of flat and more dispersive bands at the valence band maximum which dictates that these compounds may be a promising material for generating thermoelectricity, which could be an alternate source of energy to the conventional ways of producing electricity. Single perovskite $SrTiO_3$ is essentially a band insulator with an empty conduction band. Intensive electron doping under the reducing conditions, $SrTiO_3$ has power factor values of $\sim 10 \times 10^{-4} \text{ W/mK}^2$ for polycrystalline samples [38], and $20\text{--}30 \times 10^{-4} \text{ W/mK}^2$ for single crystal [39]. Heavily doping by Nb or La turns $SrTiO_3$ into an n-type degenerate semiconductor with large thermoelectric figure of merit of 0.34 at 1000 K [40]. In order to study the thermoelectric properties of double perovskite Sr_2AlMO_6 , transport properties are calculated within Boltzmann transport theory, based on the electronic structure. To obtain reliable transport properties, a dense k point mesh comprising about 5000 k points in the entire Brillouin zone was used. Calculations based on BoltzTraP code with actual band structures have proven useful in rationalizing and predicting transport properties of known compounds [17], [41] and [42]. The variation of

Seebeck coefficients at different temperatures versus the varying hole concentrations for both the compounds are given in Fig. 9(a) and (b).

increase in temperature the Seebeck coefficient increases monotonously. This behavior of increase in Seebeck coefficients with temperature is expected for large band gap materials since in these materials there is an absence of compensation between holes and electrons[43]. The Seebeck coefficients for both the compounds at different temperatures for hole concentration of 10^{19} cm^{-3} are tabulated in Table 4.

Table 4.

The Seebeck coefficients for $\text{Sr}_2\text{AlM}'\text{O}_6$ ($M' = \text{Nb}$ and Ta) compounds at different temperatures for hole concentration of 10^{19} cm^{-3} .

Temperature(K)	Seebeck coefficient ($10\mu \text{ VK}^{-1}$)	
	$\text{Sr}_2\text{AlNbO}_6$	$\text{Sr}_2\text{AlTaO}_6$
300	208.95	209.66
400	213.18	213.73
500	215.48	215.90
600	217.98	218.32
800	220.75	221.53
1000	222.08	223.01

Table options

Fig. 10(a) and (b) show the calculated power factors with respect to the relaxation time $S^2\sigma/\tau$ of $\text{Sr}_2\text{AlM}'\text{O}_6$ compounds as a function of hole concentration. The peak obtained in the figure give the direct information about the doping range, suggesting that the thermoelectric performance can be enhanced by adopting appropriate doping concentrations. The maximum value of doping concentration for $\text{Sr}_2\text{AlNbO}_6$ is $1.0051 \times 10^{21} \text{ cm}^{-3}$ and for $\text{Sr}_2\text{AlTaO}_6$ is $1.3153 \times 10^{21} \text{ cm}^{-3}$. Calculated Seebeck coefficients and $+dS/dT$ of Sr_2AlMO_6 are comparable with large band gap materials. Power factor in the usual units of W/mK^2 can be calculated by substituting the relaxation time in units of 10^{-14} s . The estimated power factor values of Sr_2AlMO_6 are about $\sim 3 \times 10^{-2} \mu\text{W/mK}^2$ which are lesser than that of polycrystalline samples of SrTiO_3 ($\sim 10 \times 10^{-4} \text{ W/mK}^2$).

6. Conclusion

In the present work, detailed investigation of the electronic structure and optical properties of $\text{Sr}_2\text{AlNbO}_6$ and $\text{Sr}_2\text{AlTaO}_6$ in the cubic phase is performed using FPLAPW method. The GGA calculated structural parameters obtained from the present study are in agreement with the experimental values. The band structure calculations shows that the valence band maximum and conduction band minimum are located at the Γ point resulting in a direct energy gap. The direct band gap of energies of $\text{Sr}_2\text{AlNbO}_6$ and $\text{Sr}_2\text{AlTaO}_6$ are 3.03 eV and 3.75 eV respectively with GGA. In order to estimate the band gap accurately, the modified Becke-Johanson potential is also used which gives a better description of the band structures and yields a significant improvement to the value of the energy gap with GGA. The calculated band gap with TB-mBJ for $\text{Sr}_2\text{AlNbO}_6$ is 3.8 eV which matches well with the experimental value.

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