BULK AND BI-LAYERED SURFACES OF $SrAlO_3$ PEROVSKITE FOR EFFICIENT SOLAR CELL APPLICATION - FULL POTENTIAL STUDY

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The structural, electronic, optical and thermoelectric properties were examined for bulk and bi-layered surface of perovskite compound namely $SrAlO_3$ by using WIEN2K code implemented from DFT(Density Functional Theory). The bi-layered surface of $SrAlO_3$ is investigated first time in our study. The structural parameters are optimized for the novel layered surface and bulk phase. The electronic properties are analyzed by using Density of States (DoS), electron density plots and band structure for both bulk and bi-layered phase. The optical parameters such as optical conductivity, photon energy and refraction are analyzed for both phases. Thermoelectric properties such as Seebeck coefficient, conductiity, powerfactor, thermoelectric figure of merit have been computed and results are agreed well with the available literature for bulk compound. All the above analysis is revealed that the layered surfaces of $SrAlO_3$ phase is predominantly favourable and effective than bulk $SrAlO_3$ for efficient energy conversion materials in solar cells.

Keywords: Thin films, Bulk structure, Wien2k, Optical properties, energy conversion

1. Introduction

The perovskite family includes all compounds whose structures are generated from an ideal perovskite type with the deletion/addition of certain atoms or with minor lattice aberrations. Perovskites are expressed with the chemical formula ABO_3. A cation is monovalent or divalent or trivalent in these perovskite compounds, whereas B cation is pentavalent, tetravalent, and trivalent. The physical characteristics of these perovskite-type compounds have grasped a lot of attention and have been widely studied in Materials Science [1-4]. $SrTiO_3$ is an interesting material to study for several reasons and mainly for thermoelectric applications. In this paper Ti is replaced by Al and the proposed formulation is $SrAlO_3$. In this order, the authors are interested to study $SrAlO_3$ as replaceable materials of versatile Strontium Titanate ($SrTiO_3$). The pervoskite phase of $SrAlO_3$ in bulk and layered surface form reported first time in our study in view of its thermoelectrical applications [5-8]. Nowadays energy demand is increasing with increasing energy requirements and environmental concerns. As a renewable green energy, the use and transformation of solar energy has become a prominent study topic. For many years, scientists have been developing solutions to help for society by using renewable/natural energy conversion materials. They are all

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looking for sustainable energy sources to replace the harmful fossil fuels. $SrAlO_3$, a crystalline substance that can be used as a "photocatalyst" in solar devices, can point us in the right way. Hence in this study the authors are concentrated to improve the efficiency of thermoelectric conversion effect by use of $SrAlO_3$ layered structures. Since layered materials has high electron density and high absorption to enhance the performance or functionality of state-of-the-art devices [9-11].

As on the literature, the Sr based layer materials namely $SrTiO_3$, $SrAl_2O_4$, $Sr_2CuO_2Cu_2S_2$ and $Sr_2CuO_2Cu_2Se_2$ are experimentally synthesized in laboratory and widely used in industrial scale applications including photo refractive, photovoltaic, ferro electricity, growth substrate for high temperature superconductor thin films, Photo catalyst, grain-boundary barrier layer capacitors, oxygen-gas sensors and optical switches etc., [12-16]. At 18 a.u distance between two layers of $SrAlO_3$, each layer has a complete chemical structure without dangling bonds, which makes each individual layer relatively stable. Layered materials have emerged as promising candidates for next-generation electronic and optoelectronic applications. In just a decade, these layered materials have expanded into a vast range of applications in diverse areas of technology such as optoelectronics, Solar cell applications, spintronics, catalysis, energy harvesting and storage, ion transport, and biomedicine etc., In this study in view of solar cell application the electronic, optical and thermoelectric properties are investigated for the proposed material. One of the challenging milestones to integrate these layered materials into commercial devices lies in the development of synthesis methods that provide reliable control of the crystalline quality and orientation over large areas, as well as the engineering of defects and crystal phases. In this regard, monolayer of $SrAlO_3$ have been synthesized on bi layer of graphene using molecular beam epitaxy.

2. Materials and Methodology

The $SrAlO_3$ phase in bulk and thin filmed surface are investigated using one of the first principle code WIEN2K. The code initially starts from structure generating document comprising information on space group, lattice

The $SrAlO_3$ phase in bulk and thin filmed surface are investigated using one of the first principle code WIEN2K. The code initially starts from structure generating document comprising information on space group, lattice parameters, atomic species, atomic location, muffin tin radii, etc [17-19]. The initialization computations are performed with energy and charge convergence parameter, RMT * Kmax which controls the size of the baris set is set to 7 with 1000 optimized k-points. The bulk crystal structure of $SrAlO_3$ is belong to the space group is Pm-3m_221 (cubic primitive) with lattice constant 7.2575 a.u and the

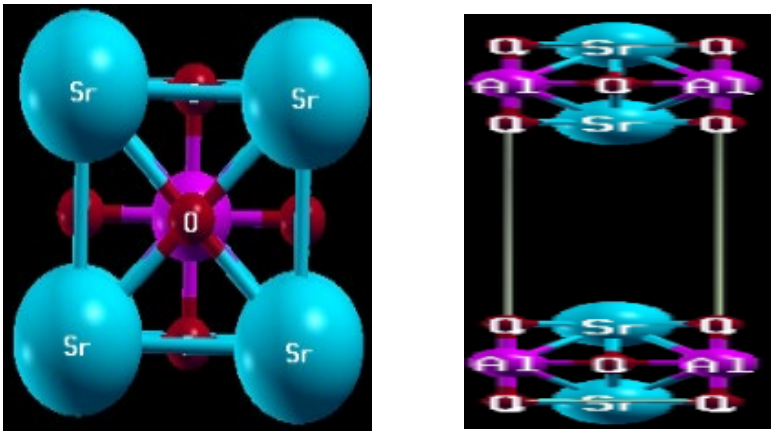
position of the atoms are Sr (0,0,0) ; Al (0.5,0.5, 0.5) ; O (0, 0.5, 0.5) [20]. In this study, in addition to Bulk $SrAlO_3$, the layered $SrAlO_3$ phases are formulated first time in our study. Cut off energy is -6 Rydberg and a self-consistent energy convergence criterion is 0.0001 Rydberg. The equation of states is derived by using Birch Murnaghan [21].

The thermoelectric properties are analyzed by using the semi classical (Boltzmann) transport equation at constant relaxation time can be solved using BoltzTraP code [22]. This BoltzTraP code was used to calculate electrical conductivity (σ), Seebeck coefficient (S) and thermal conductivity (K). S is independent of relaxation time (τ) and hence σ and κ are derived in the units of τ. To analyze the optical properties of the proposed materials refractive index, reflectivity, optical conductivity and photon energy are computed and analyzed.

3. Results and Discussion

3.1 Structural Properties

Initially the structure file was generated for $SrAlO_3$ by using experimental lattice constants and position of the atoms [20]. The total energy of the given system is obtained and then fitted into the Birch-Murnaghan equation of state. As a result, with a stabled energy, optimized lattice constant is computed. The optimized bulk and bi-layered crystal structure of $SrAlO_3$ is given in Fig. 1a. The bi-layered structure of $SrAlO_3$ is about two layers of $SrAlO_3$ are separated with 18 a.u (Fig. 1b). The corresponding structural data is reported in Table 1. There is a phase transformation taken place from the bulk cubic structure to layered tetragonal structure from bulk to layered formulation.



(a) (b)

Fig. 1 Crystal structure of (a) Bulk and (b) bi- layered surface phase of $SrAlO_3$

3.2 *Electronic properties*

Density of states (DoS) histograms and band structure plots are often provide sufficient information about the electronic properties of a material. The band structure and DoS histograms for the optimized bulk and layered structures are plotted and reported in Fig. 2 and Fig.3 respectively. The corresponding electronic parameters are presented in Table 1. These plots are plotted by the supporting programs of WIEN2k software. These plots are drawn using Fermi energy, total ($SrAlO_3$) and partial (Sr, Al, O) density of states in Fig.2. It is observed that electrons from 'O' atom contributes more than electrons from Sr and Al towards density of states (number of electrons at Fermilevel). Hence Fig.3 plotted for individual O contribution towards total DoS for bi layered $SrAlO_3$. The mobility of the electrons over the Fermilevel, is the evidence for the conducting nature of the proposed materials. The authors are observed that DoS is increases from around 42 Rydberg (bulk) to 96 Rydberg (Layers with 18 a.u distance) since there is an increment of contributing electrons over Fermi level. In $SrAlO_3$ bulk crystals, the major contribution is arising from O atoms and is about 31.68 Rydberg. In $SrAlO_3$ layered formulation, the oxygen atoms contribution is around 81 Rydberg out of 96 Rydberg.

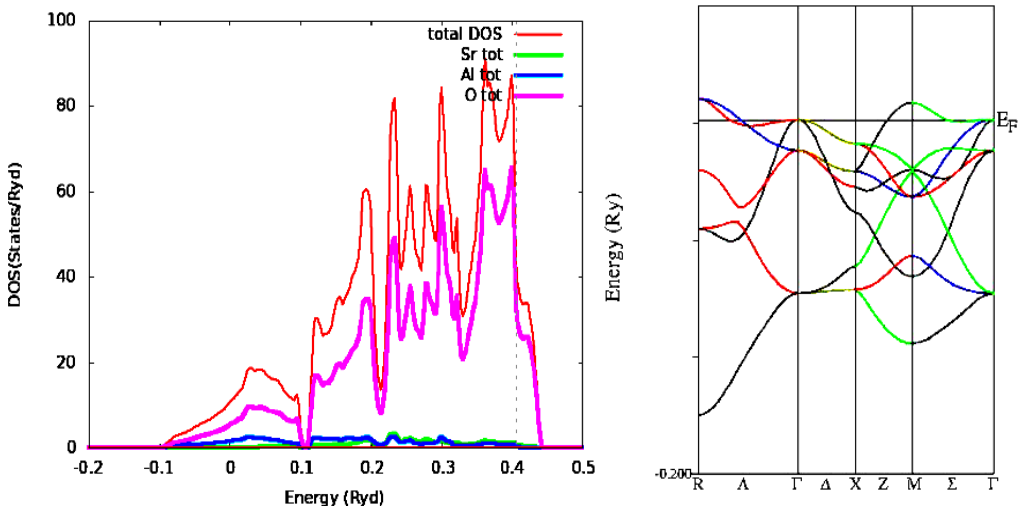
Structural and electronic parameters

Table 1

Parameter	**$SrAlO_3$ - Bulk Crystal structure**	**Two layers of $SrAlO_3$ separated by 18 au**
Optimized Lattice constant (a.u.)	a=b=c=7.257496 (a=7.489) [20]	a=b=7.2575 c=33.4120
Space group	221 (Pm-3m)	123 (P4/mmm)
Lattice type	Cubic Primitive	Tetragonal Primitive
Electronic nature	Conductor (Band gap is 0 eV)[20]	Conductor
Fermi Energy (Ryd)	0.4057	0.1311
Electronic specific heat coefficient (C_V) J/(kg K)	7.29	16.63
Total DOS ($N(E_F)$) Ryd	42.07	96
No. of Electrons contributing for thermoelectric/ conducting property	37	90

The density of states (DoS) is essentially the number of different states at a particular energy level that electrons are allowed to occupy, the number of

electron states per unit volume per unit energy. Band structure plots shows the electron transport nature over Fermi level. As we can see in the Fig. 2a and 3a, the graphs indicate the density of state (DoS) increases from bulk to layered $SrAlO_3$ structures. In both cases the contribution from Oxygen is higher than other atom. DoS histograms depicts the conducting nature of both phases, since absence of energy gap and the bands are overlapping from valence band to conduction band through Fermi level. The available literature [20] shows good agreement with our results. $SrAlO_3$ layers with distance 18 a.u. predominantly shows a strong electron correlation effect, which is observed in Fig. 3 and the same exhibits conducting nature of layered phase. The bands are well overlapped at M and R points (Fig.3b). The valence band for $SrAlO_3$ in Fig.3 DoS and band profiles are contributed by O-p state, with additional contributions from the Al-d, Al-p, and Sr-d states. The bands in the conduction band are caused by the Al-d and Sr-d states, with a minor contribution from the O-p states. O-p states make up the majority of the valence band, while Al-d and Sr-d states make up the majority of the conduction band. Thus, layered phase of $SrAlO_3$, DoS is more than bulk $SrAlO_3$, hence layered $SrAlO_3$, may one of the potential candidate for energy conversion application. The other possibilities are investigated in upcoming analysis.



(a) (b)

Fig 2 (a) Total and partial DOS and (b) band structure of bulk cubic $SrAlO_3$.

Electron density plots are plotted for the optimized bulk and layered structures and reported in Fig. 4 (a) and (b) respectively to understand the electron mobility and bonding nature between the atoms. In Fig. 4. Oxygen atom is located beside Al atom. There is an existence of ionic bonding between Sr and Al/O. The

bonding becomes stronger in layered phase of $SrAlO_3$, Since the Contours around the atoms are closer and large in number in Fig. 4b. The same is one of the supporting bonding nature for efficient perovskite material.

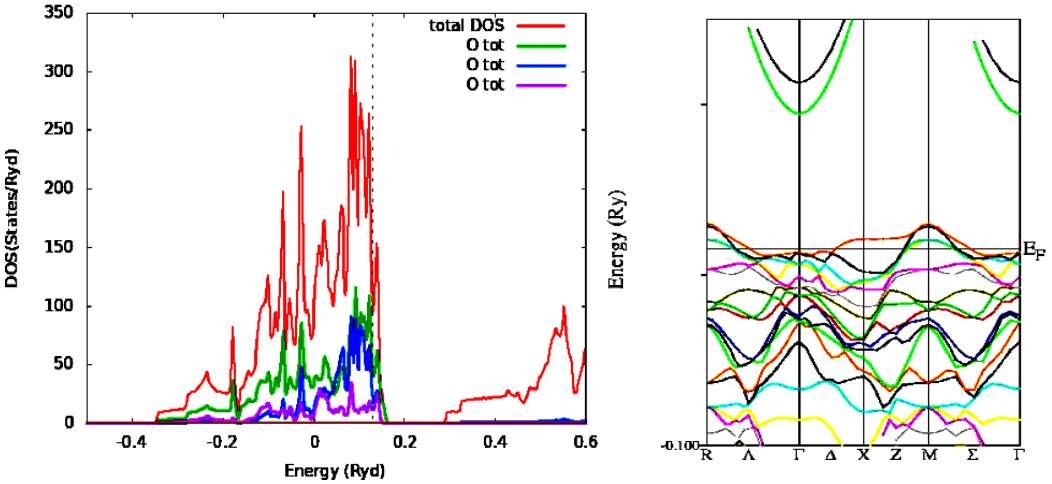


Fig 3 (a) Total and partial DOS and (b) band structure of bi-layered phase of $SrAlO_3$

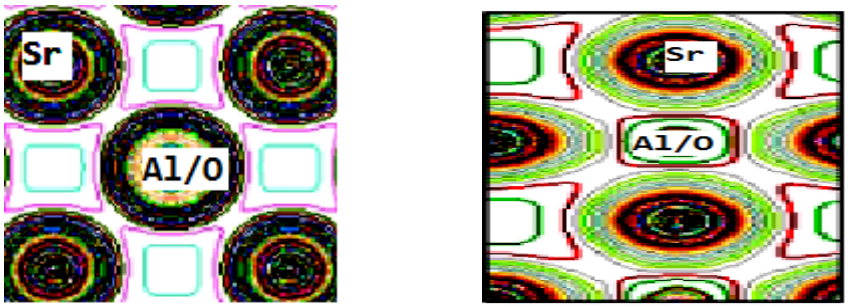
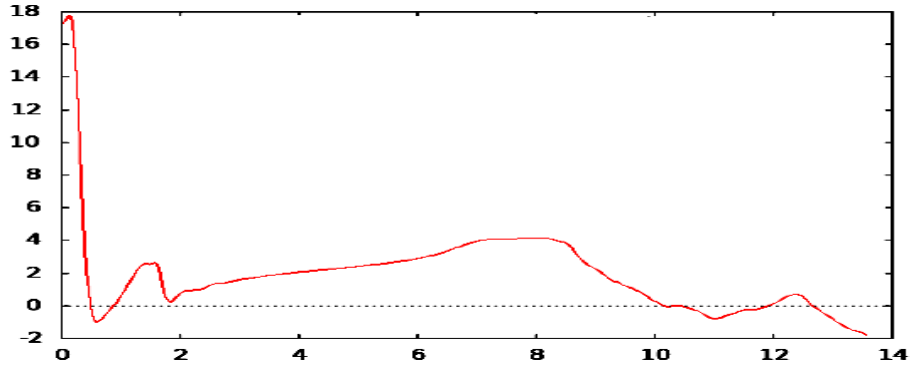


Fig 4 Electron Density plot (a) Bulk $SrAlO_3$ (b) bi-layered phase of $SrAlO_3$

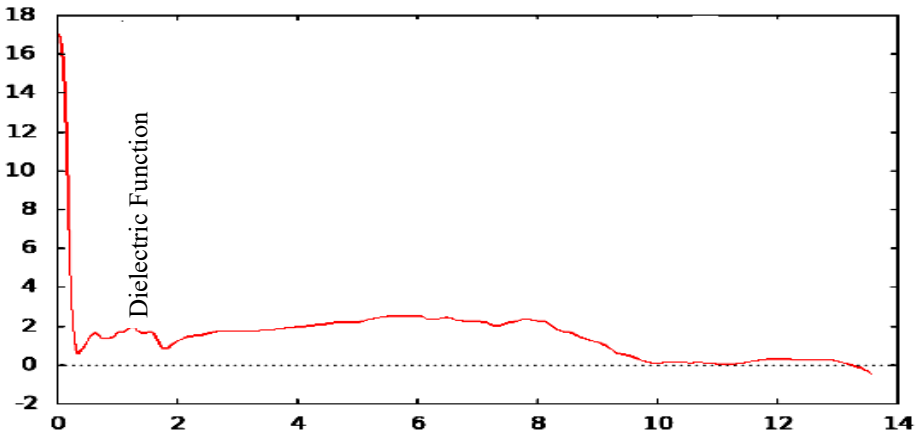
3.3 Optical properties.

Fig. 5a and 5b is plotted in between Photon Energy (x-axis) Vs dielectric function (y axis) for bulk and layered phases respectively in the range from 0 to 14 eV. Evaluating the peaks of the dielectric function (ε) and the corresponding Energy from the Fig. 5 will explain the nature of transitions related to the optical spectra. From the graph it can be seen all formulations are optically good and dielectric function is one of the tool to get an idea about photon absorption of proposed materials. Fig. 6a and 6b is plotted in between Photon Energy (x-axis) Vs optical conductivity (y axis) for bulk and layered phases respectively. Optical

Conductivity σ(ω) describes the conduction charges over a particular range of Photon energy are given in Fig. 5 for bulk and layered $SrAlO_3$ materials. The main peak of σ(ω) is at 8-10 and 12-14 eV in both the formulations. There are many minor peaks exhibit excitonic feature and the same implies that these formulations have more photons (energy) absorbent which one of the favorable property for efficient solar cell material. Photon energy Vs Refraction (Fig.7) are plotted for bulk and layered phases of $SrAlO_3$. The stabilized refractive index, is about 4.1 for layered material, whereas 4.3 for bulk material, which is higher than layered phase. The low refraction induces more photonic effect, and it leads to absorbs more energy [23-25]. From all the above observations, it can be concluding that $SrTiO_3$ layered phase has remarkable sign for good solar cell material based on its optical properties. Hence these materials are suitable to absorb high photo energy, which is suitable to efficient energy conversion materials.

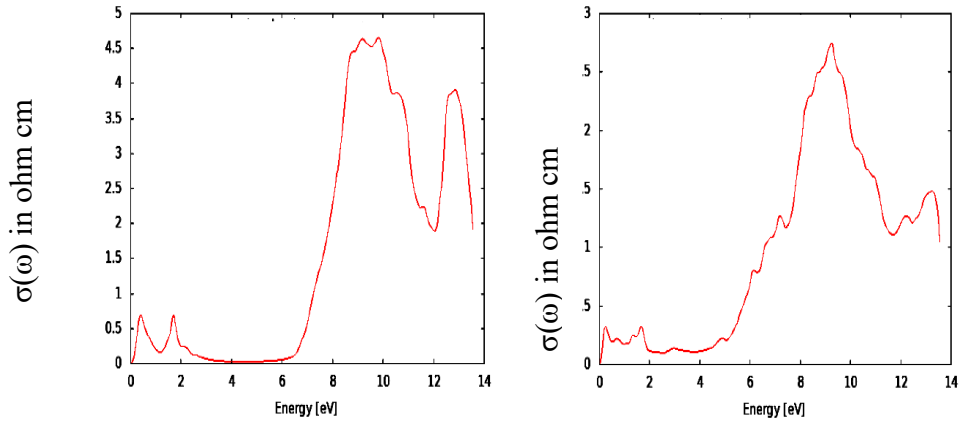


(a)



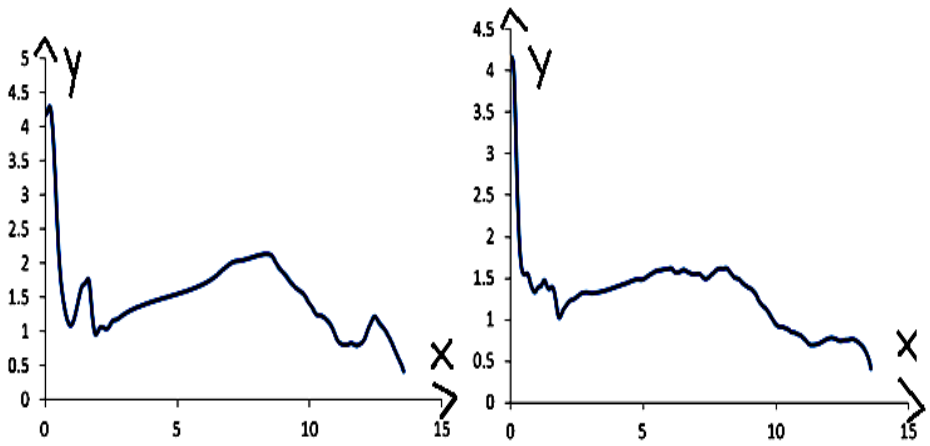
(b)

Fig. 5 Photon Energy (x-axis) Vs dielectric function (y axis) of $SrAlO_3$
(a) Bulk Phase (b) Bi-Layered Phase



(a) (b)

Fig. 6. Photon Energy (x-axis) Vs Optical Conductivity σ(ω) (y axis) of $SrAlO_3$
(a) Bulk (b) bi- layered Phase



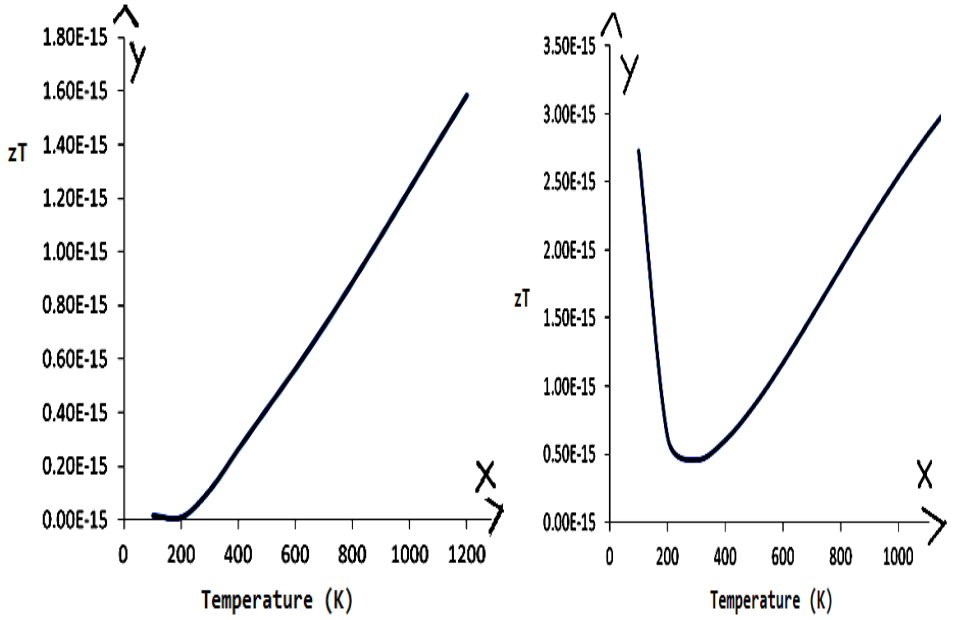
(a) (b)

Fig. 7. Photon Energy (x-axis) Vs refraction (y axis) of $SrAlO_3$
(a) Bulk (b) bi-layered Phase

3.4 ***Thermoelectric properties***

The thermoelectric efficiency is one of the most important tool for solar cell materials. The computed thermoelectric parameters from 100 K to 1200 K of the bulk and layered phases are presented in Table 2. The computed Seebeck coefficient and conductivity of parent compounds of our study shows that good agreement with the available experimental data. Seebeck coefficient 'S' is positive when the hole contribution is larger and 'S' is negative when the electron transport contribution is higher. In these formulation the hole contribution is more than electrons. The observed power factors ($S^2\sigma$) are strengthening the good

conducting nature of proposed compounds. To carry on thermoelectric figure of merit (ZT), it is calculated by using the relation $ZT= \sigma S^2T /k$ and it is plotted as a graph in Fig. 8. From the results it is observed that the ZT values are less than unity. In addition, they are in the order of 10^-15



(a) (b)

Fig. 8. Temperature in K Vs zT (dimensionless figure of merit) of $SrAlO_3$
(a) Bulk (b) bi-layered Phase

The thermoelectric figure of merit (zT) value, Electrical conductivity (σ), Seebeck coefficient (S) and power factor ($S^2\sigma$) for an optimized bulk and layered structure are computed and reported in Table 2. The observed range of power factor 6.94E-05 - 8.43E-03 [$\mu W/(cm\ K^2)$] in bulk phase and 7.63E-14 to 1.07 E-12 in layer phase shows that the proposed materials has effective energy conversion efficiency in view of thermoelectric property. As layered phase having effective thermoelectric efficiency due to strong intra layer and weak interlayer bonding nature than bulk phase. In addition, the supporting reasons to conclude the efficiency of layered material than bulk $SrAlO_3$ phase are (i) The optimized state represented by a curve like parabolic. Fig 8b is more parabolic than Fig. 8a, since the efficient thermoelectric figure of merit with respect to temperature of the layered materials. (ii) At and near room temperature Bulk phase (Fig.8a) zT falls to zero but Layered phase (Fig.8b) exist with a considerable value and attains maximum value at high temperature.

The Seebeck coeffcient (S), electrical conductivity (σ), power factor (P), for bulk and bi-layered phases of $SrAlO_3$ at ambient and low/high temperature

Table 2

T (K)	$SrAlO_3$ (Bulk)			$SrAlO_3$ (Bi-Layer)		
	S (μV/K)	σ ($\Omega^{-1}m^{-1}$)	P [μW/(cm K^2)]	S (μV/K)	σ (Ω^{-1} m^{-1})	P [μW/(cm K^2)]
100	9.42E-06	7.82E+05	6.94E-05	7.70E-05	7.70E-05	4.57E-13
200	6.59E-06	1.22E+06	5.31E-05	3.79E-05	3.79E-05	5.43E-14
300	2.08E-05	1.45E+06	6.31E-04	3.52E-05	3.52E-05	4.36E-14
400	3.06E-05	1.55E+06	1.45E-03	4.24E-05	4.24E-05	7.63E-14
500	3.74E-05	1.60E+06	2.25E-03	5.19E-05	5.19E-05	1.40E-13
600	4.33E-05	1.63E+06	3.06E-03	6.16E-05	6.16E-05	2.34E-13
700	4.87E-05	1.65E+06	3.92E-03	7.08E-05	7.08E-05	3.55E-13
800	5.38E-05	1.67E+06	4.83E-03	7.92E-05	7.92E-05	4.96E-13
900	5.86E-05	1.68E+06	5.76E-03	8.65E-05	8.65E-05	6.47E-13
1000	6.29E-05	1.69E+06	6.69E-03	9.27E-05	9.27E-05	7.98E-13
1100	6.68E-05	1.70E+06	7.58E-03	9.79E-05	9.79E-05	9.39E-13
1200	7.03E-05	1.70E+06	8.43E-03	1.02E-04	1.02E-04	1.07E-12

4.Conclusion

The thorough analysis is made in both of its bulk and layer phase of $SrAlO_3$ structures with respect to their structural, electronic, optical, and thermoelectric properties. From the structural properties there is existence of phase transition from cubic to tetragonal primitive from bulk to layered phases respectively. In view of electronic and optical properties, density of states (DOS), band structure, optical efficiency of phonon transfers and it is highly noticed in layered formulation of $SrAlO_3$ with 18 a.u distance between two $SrAlO_3$ layers. The thin film of $SrAlO_3$ will be more efficient materials for light energy to electrical energy conversion application. In the energy range of 0 to 14 eV, optical parameters like the dielectric constant, refractive index and optical conductivity were studied for both bulk and layered phases. Thus, this formulation of $SrAlO_3$ layered structure again proved its efficiency towards energy conversion property

due to its more absorption of solar energy. In order to look into computed thermoelectric figure of merit of these reported materials, it shows that these materials are effective to thermoelectric energy conversion efficiency. Especially $SrAlO_3$ Bi-Layered structured perovskites have titanic potential for novel solar cells applications than reported bulk material.

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