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ARTICLE

Thermoelectric Properties of $ALiF_3$ (A= Ca, Sr and Ba): First-Principles Calculation

Nada T. Mahmoud[a], **Ahmad A. Mousa**[b] **and Jamil M. Khalifeh**[a]

[a] *Physics Department, The University of Jordan, 11942-Amman, Jordan.*
[b] *Middle East University (MEU), 11831-Amman, Jordan.*

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Abstract: The energy band structure obtained from WIEN2k calculations is used to calculate the transport coefficients *via* the semi-classical Boltzmann transport theory with constant relaxation time (τ) as employed in the BoltzTraP package for $ALiF_3$(A= Ca, Sr and Ba) using mBJ-GGA potential. The thermoelectric properties of the above compounds are investigated through the calculation of the main transport properties: Seebeck coefficient (S), electrical (σ) and electronic thermal (k_e) conductivity, figure of merit (ZT) and power factor. All compounds show insulating behavior.

Keywords: Fluoroperovskite, Band gap, BoltzTraP, Thermoelectric properties, Figure of merit.

Introduction

Searching for new materials with efficient thermoelectric (TE) properties has attracted great interest from researchers in order to obtain a better conversion of energy from waste heat to electricity [1, 2]. To date, it has been shown that many classes of material have promising TE properties, such as complex oxides [3, 4], Skutterudites [5, 6], Clathrates [7, 8] and half Heusler [9, 10].

We previously investigated the optical and electronic properties of $XLiF_3$ (X = Ca, Sr and Ba) using first-principles calculation. The study has shown the presence of a direct band gap (Γ-Γ) [11]. Furthermore, we have shown that the electronic, structural, optical and magnetic properties of $SrLiF_3$ compounds have been changed by inserting Eu ions in Sr sites [12].

Perovskite compounds have an interesting history of being considered for thermoelectric applications due to their low thermal conductivity and high Seebeck coefficient. Some of perovskite materials can be used as an alternate source for renewing waste heat caused by industries. In a very recent investigation, the electronic, structural and thermoelectric transport properties of $KCaF_3$ compounds by ab-initio method were studied. The calculated electronic structures indicated that $KCaF_3$ is an insulator [13].

Calculation Method

We performed self-consistent calculations based on density functional theory (DFT) [14] using the full-potential linearized augmented plane wave (FP-LAPW) approach as implemented in the Wien2k package [15]. In this approach, we partitioned the unit cell into two regions: the first is atomic muffin-tin centered spheres with radii RMT and the second is interstitial region [16]. The exchange and correlation potential is used within the modified Becke-Johnson (mBJ) [17]. Our compounds are in Pm-3m (#221) space group with a cubic structure. The maximum quantum number ℓ for the wave function expansion inside the atomic

Corresponding Author: Jamil M. Khalifeh **Email**: jkalifa@ju.edu.jo

muffin-tin spheres is taken up to ℓmax =10. The core cut-off energy is -6 Ry and the plane wave cut-off 16 Ry is chosen for the expansion of wave functions in the interstitial region. The charge density is Fourier expanded up to Gmax = 12. For the Kmesh sampling, we used the 14×14×14 mesh of points for structural and electronic properties' calculations. The lattice parameters are calculated using the Murnaghan's equation of state [18]. The calculations are carried out self-consistently and the results are taken when the convergence tolerance of charge is less than 10^{-4} electron charge.

Band structure energies obtained from WIEN2k calculations, using mBJ approximations, enable us to calculate the transport properties of $ALiF_3$ (A= Ca, Sr and Ba). The different transport coefficients are calculated using the semi-classical Boltzmann transport theory within the constant relaxation time (τ) approximation as employed in the BoltzTraP computer package [19, 20]. Dense k-mesh of 40×40×40 in the full Brillouin zone is used to gain meaningful results. The main transport coefficients are electrical conductivity (σ), electronic thermal conductivity (K_e) and Seebeck coefficient (S). They are given by the following formulae [21]:

$$\sigma = e^2 \int dE \left(\frac{\partial f_o}{\partial E}\right) \sum(E) \tag{1}$$

$$K_e = \frac{1}{T} \int dE \left(-\frac{\partial f_o}{\partial E}\right) \sum(E)(E-\mu)^2 \tag{2}$$

$$S = \frac{e}{\sigma T} \int dE \left(-\frac{\partial f_o}{\partial E}\right) \sum(E)(E-\mu) \tag{3}$$

where,

$$\left(-\frac{\partial f_o}{\partial E}\right) = \frac{1}{K_B T} \frac{\exp(\frac{\varepsilon-\mu}{K_B T})}{(\exp\left[\left(\frac{\varepsilon-\mu}{K_B T}\right)\right]+1)^2} \tag{4}$$

and ∑(E) is the transport distribution function given by [21]:

$$\sum(E) = \frac{2}{3} \int \frac{d^3k}{(2\pi)^3} \upsilon_k^2 \tau(k) \delta\left(E - E_c - \frac{\hbar^2 k^2}{2m_e^*}\right). \tag{5}$$

Here, υ_k and m_e^* are the velocity and the effective mass of the electron in the conduction band, respectively. E_c is the minimum energy of the conduction band.

In the general case, TE's efficiency is characterized by the dimensionless figure of merit ZT. It determines the thermoelectric performance of materials. In other words, the material having better TE performance has larger ZT value [21], defined as:

$$ZT = \frac{\sigma S^2}{K_e + K_l} T \tag{6}$$

where, k_e+k_l and T are the total thermal conductivity K and temperature, respectively. For practical applications, materials with ZT ≥ 1 are required. Larger ZT requires greater σ and smaller *K* (total thermal conductivity) for good practical thermal electric system.

Results and Discussion

Band Gap and Density of States

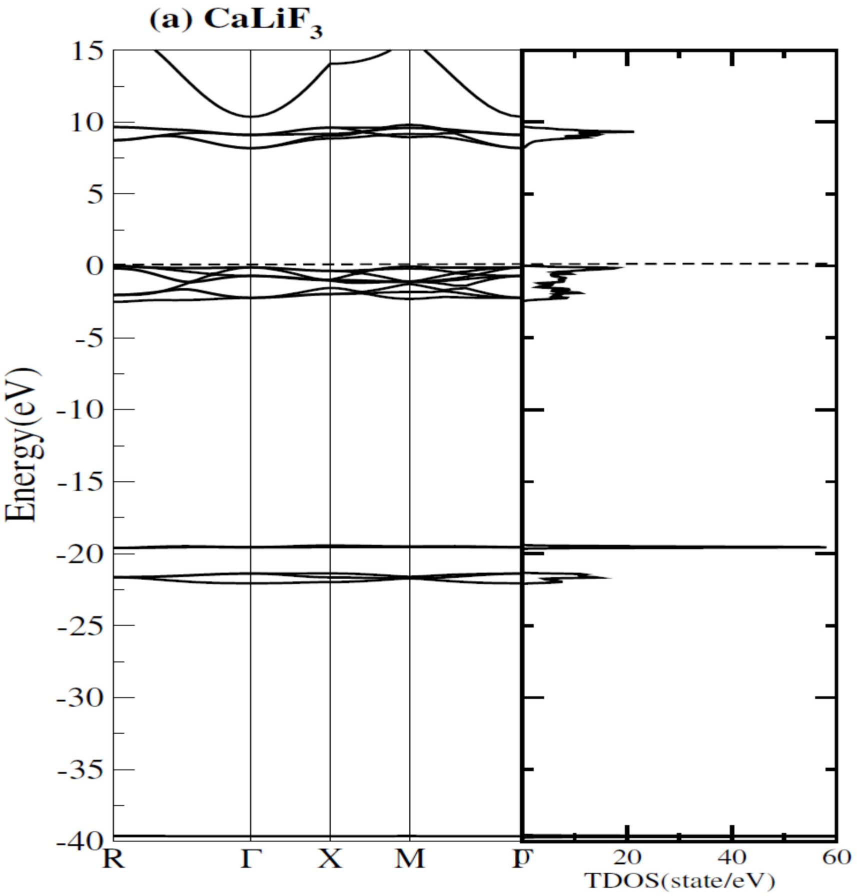
Our previous band structure calculations through DFT indicated that the three perovskite systems $ALiF_3$ (A= Ca, Sr and Ba) are insulators using GGA approximation [11] and mBJ-GGA potentials [22, 23] and the energy band gap (E_g) values are: 8.202eV, 9.399eV and 8.199eV for $CaLiF_3$, $SrLiF_3$ and $BaLiF_3$, respectively.

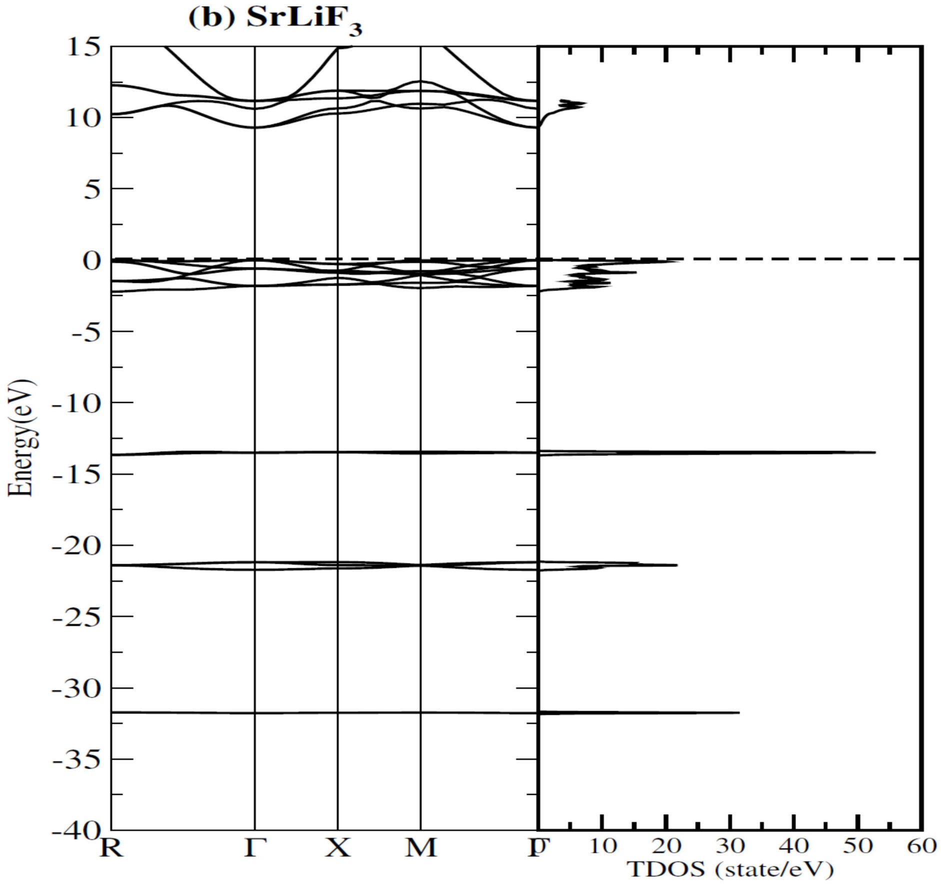
Fig.1 shows the band structure and density of states for the investigated systems. The energy band gap (E_g) is found to be direct (Γ–Γ) for both $SrLiF_3$ and $BaLiF_3$ compounds and indirect (M–Γ) for $CaLiF_3$.

Thermoelectric Properties

Using the energy eigenvalues obtained from the DFT calculations by solving the Boltzmann semi-classical equation with constant relaxation time (τ) approximation using the BoltzTrap computer packages, we investigate the electronic transport coefficients. The calculated coefficients are: the electrical conductivity (σ/τ), thermal conductivity (κ/τ), Seebeck coefficient (S), figure of merit (ZT) and power factor as a function of temperature.

The electrical conductivity (σ/τ) is displayed for CaLiF3, $SrLiF_3$ and $BaLiF_3$ compounds in Fig. 2. It is obvious that electrical conductivity is a function of temperature; this is a typical behavior of insulators [19]. All compounds indicate minimum value of (σ/τ) at low temperature (50 K) equal to 0.591×10^{18}(1/Ω.m.s), the maximum values reach 26.732 $\times10^{18}$(1/Ω.m.s), 38.000 $\times10^{18}$(1/Ω.m.s) and 30.232 $\times10^{18}$(1/Ω.m.s) at 800K temperature for $CaLiF_3$, $SrLiF_3$ and $BaLiF_3$, respectively. The electrical conductivity calculation agrees with band structure calculations (Fig. 1).


(a) CaLiF$_3$
Energy(eV)
15
10
5
0
-5
-10
-15
-20
-25
-30
-35
-40
R
Γ
X
M
Γ
20
40
60
TDOS(state/eV)


(b) SrLiF$_3$
Energy(eV)
15
10
5
0
-5
-10
-15
-20
-25
-30
-35
-40
R
Γ
X
M
Γ
10
20
30
40
50
60
TDOS (state/eV)

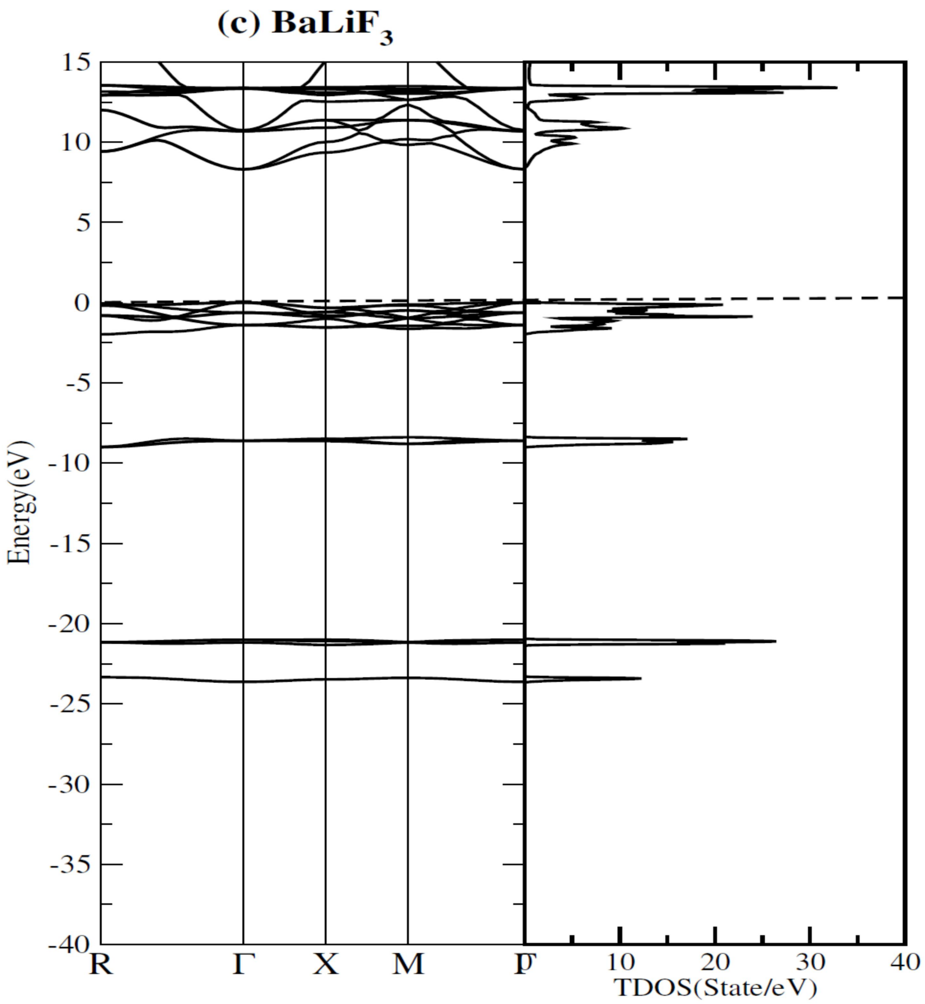


FIG. 1. Electronic band structure and density of states (a) CaLiF$_3$, (b) SrLiF$_3$ and (c) BaLiF$_3$.

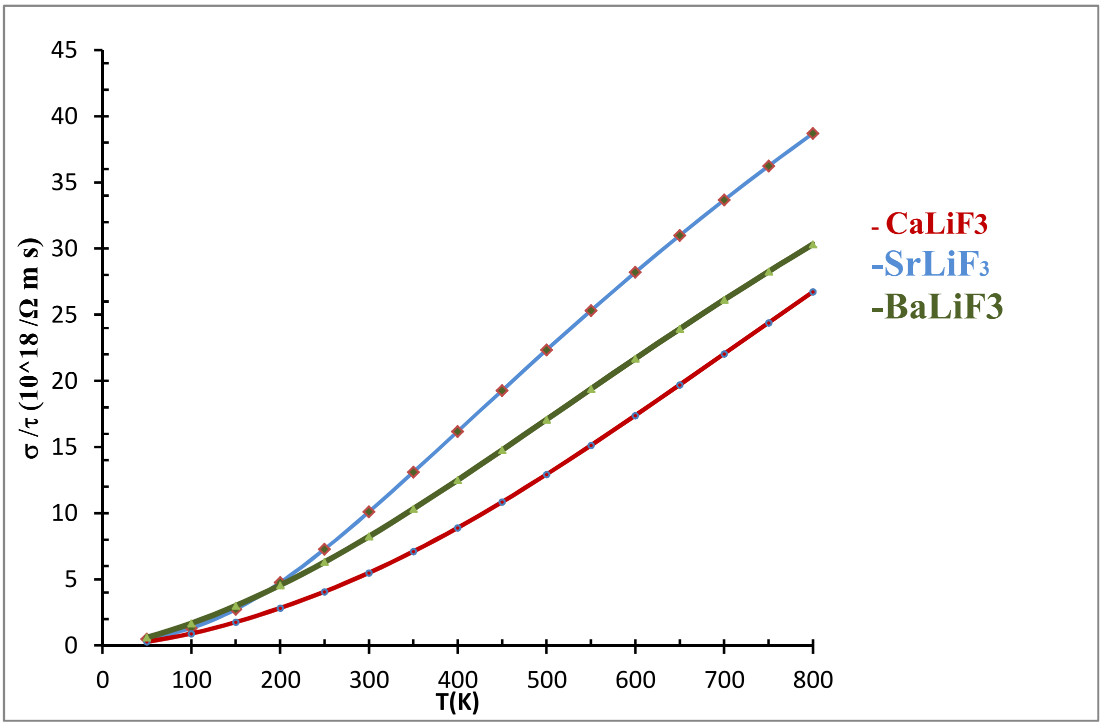


FIG. 2. Electrical conductivity, σ /τ (10^{18} / Ω.m.s).

In our calculations, CaLiF3, SrLiF$_3$ and BaLiF$_3$ show thermal insulating behavior, where thermal conductivity k_e/τ increases as temperature increases (Fig. 3). The increase in k_e/τ arises from heating material which increases atomic vibrations to a limit such that they transmit energy in the form of kinetic energy. The values of k_e/τ, at the whole range of temperature, for both CaLiF$_3$ and BaLiF$_3$ compounds are comparable, since E_g for both of them is almost equal. At low temperature (zero Kelvin), the material is an insulator (8.202eV, 9.399eV and 8.199eV for CaLiF$_3$, SrLiF$_3$ and BaLiF$_3$, respectively). The total thermal conductivity (k_e+k_l) increases at high temperature. The contribution of the lattice thermal conductivity (k_l) resulting from phonon-phonon interaction is responsible of the total thermal conductivity. Thermal conductivity here is due to the electronic part only, which is equal to 3.2 (W/ m.K), 1.9 (W/ m.K) and 1.2 (W/ m.K) for SrLiF$_3$, BaLiF$_3$ and CaLiF$_3$, respectively, at T=300 K. If k_l were (not calculated here) considered in the calculations, then the estimated total K would be larger than k_e. As a result, ZT value is expected to be smaller than the observed one [24, 25]. That is; the total thermal conductivity is enhanced by increasing temperature.

Fig. 4 illustrates the temperature dependence of Seebeck coefficient. The S values for CaLiF$_3$ and BaLiF$_3$ show very small decrement after 300K, and almost constant in all the range of temperature for CaLiF$_3$ perovskite.

SrLiF$_3$ perovskite shows a decreasing trend of S value beyond 300K (room temperature) which is a typical behavior for insulators in agreement with band structure calculations. The minimum value of S is found at 50K for all compounds. Meanwhile, the maximum value of Seebeck coefficient occurs almost at room temperature (300K), as listed in Table (1).

TE efficiency of the device can be described in terms of ZT. For practical applications, ZT ≥ 1 for good heat conversion [17]. ZT for both CaLiF$_3$ and BaLiF$_3$ show a small increase beyond 300K. On the other hand, ZT value of SrLiF$_3$ tends to decrease beyond 300K; one can notice this behavior clearly in Fig. 5. The value of ZT at room temperature (300K) for the three compounds is presented in Table 1; it is obvious that ZT values are less than one.

Using the values of (S) and (σ/τ), one can calculate the power factor ($S^2\sigma$). The electric power factor is reported in Fig.6. The power factor increases monotonically with the increase in temperature from 100K to 800K for all compounds. The maximum value of the calculated power factor is 1.480×10^{12}(W/mK^2), 1.630×10^{12}(W/mK^2) and 1.340×10^{12}(W/mK^2) for CaLiF$_3$, SrLiF$_3$ and BaLiF$_3$, respectively.

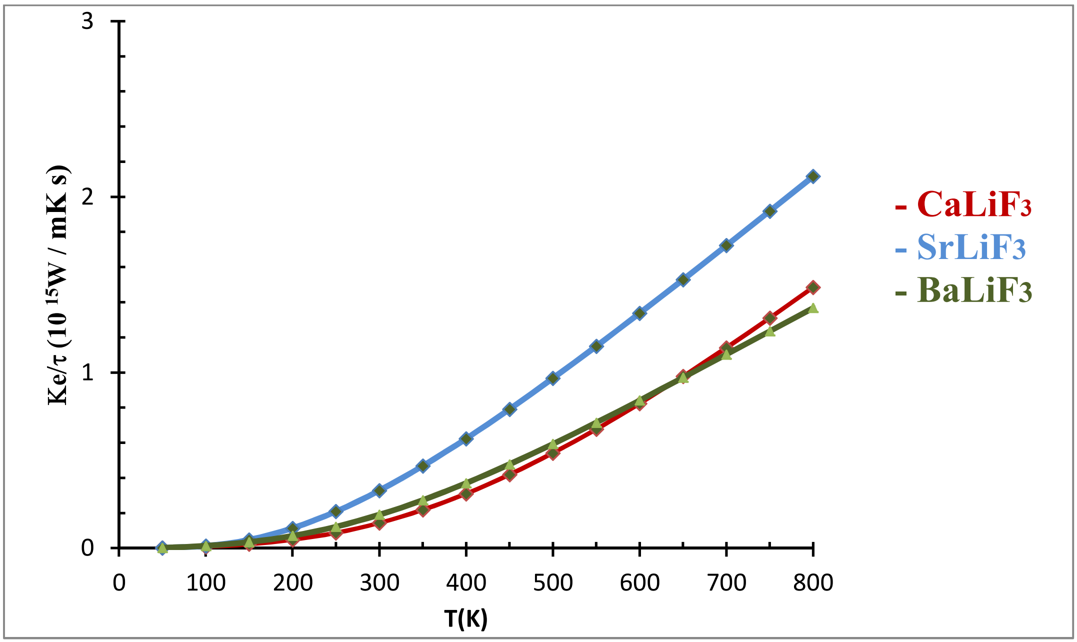


FIG. 3. Electronic thermal conductivity, K_ε/τ (10^{15} W / m K s).

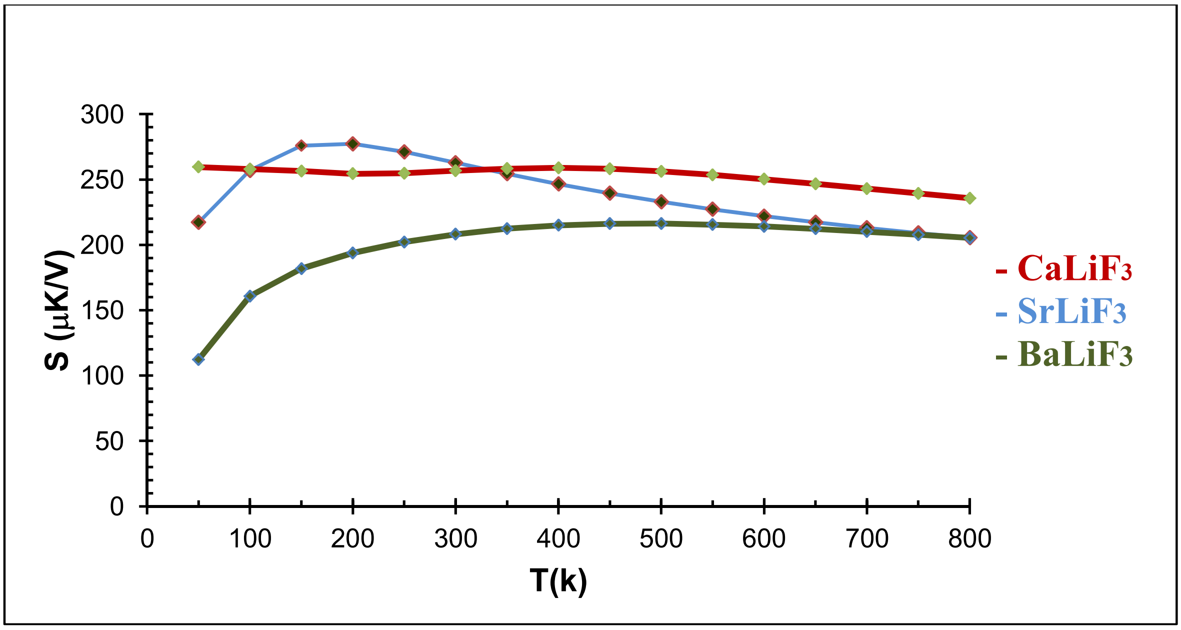


FIG. 4. The Seebeck coefficient (μV/K).

TABLE 1. Seebeck coefficient (μV/K) and figure of merit ZT at room temperature 300K.

Compound	Seebeck Coefficient (μV/K)	Figure of merit ZT
$CaliF_3$	256.665	0.758
$SrLiF_3$	262.778	0.806
$BaLiF_3$	241.480	0.757

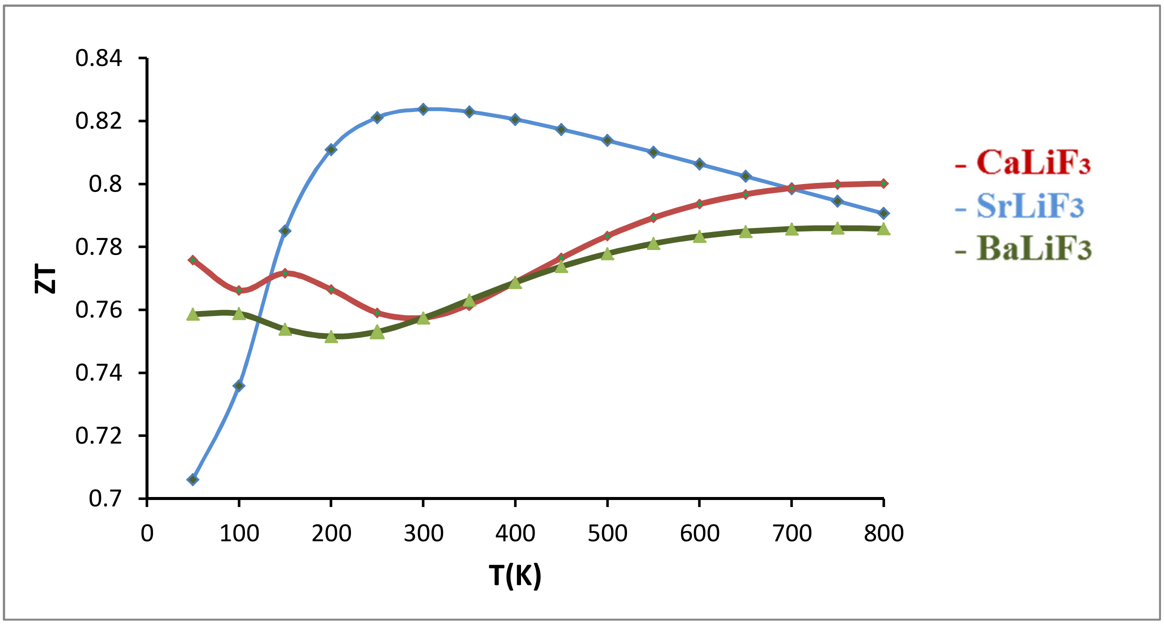


FIG. 5. The figure of merit (ZT).

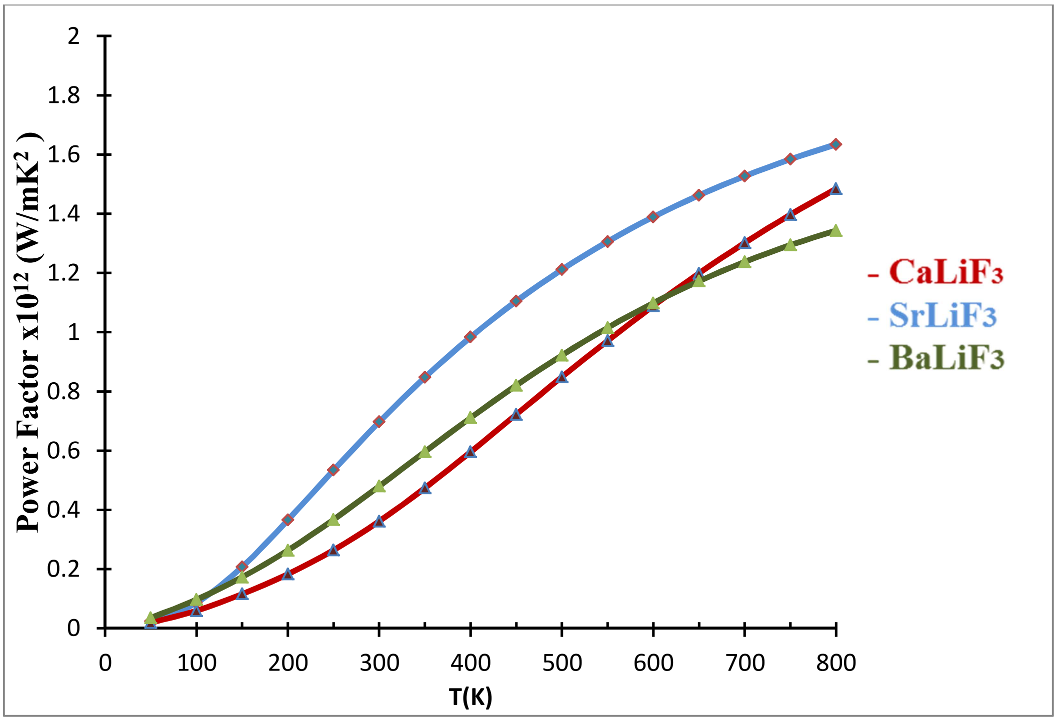


FIG. 6. The power factor (10^{12}W/mK^2).

Conclusion

Thermoelectric properties of ALiF$_3$ (A= Ca, Sr and Ba) perovskite are calculated using the energy eigenvalues obtained from the DFT calculations by solving the Boltzmann semi-classical equation using the BoltzTrap code. The calculations of the (σ/τ) and (κ/τ) as a function of temperature are found in agreement with band structure calculations. Meanwhile, Seebeck coefficient (S) is also calculated for the three systems. The results show that the S value is decreasing with temperature above 300K for all compounds. The values of S for all systems are calculated at 300K.

TE efficiency is characterized by the dimensionless quantity ZT, the value of ZT is almost constant above 300K for BaLiF$_3$ and increases with temperature for CaLiF$_3$ compound, while it decreases with temperature for SrLiF$_3$.

Although it is often supposed that TE devices made of materials with a higher power factor are capable of generating more energy, this is only true for a thermoelectric device with fixed geometry and unlimited heat source and cooling. If the geometry of the device is designed for specific application, the maximum functionality of TE materials will be determined by their ZT, not $S^2\sigma$ [26]. The investigated systems are not suitable for TE devices, as they act as insulators.

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