First Principles Study of Electronic and Thermoelectric Performance of Li Intercalated $MoSe_2$ Nanotubes

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Abstract. We present a comparative study of pristine and Li intercalated $MoSe_2$ nanotube of armchair (6, 6) and zigzag (10, 0) chirality within the framework of density functional theory (DFT). Pristine nanotube is found to have band gap which vanishes upon Li intercalation. Additionally, Li intercalation results in reduction of room temperature ZT_e for armchair $MoSe_2$ nanotube and enhancement in ZT_e for intercalated zigzag $MoSe_2$ nanotube as compared to respective pristine nanotubes. Our results suggest that Li intercalation leads to a relatively high Seeback coefficient which may enhance the thermoelectric performance of zigzag $MoSe_2$ nanotube.

Keywords: DFT, Electronic Properties, Thermoelectric Properties.
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INTRODUCTION

Transition metal dichalcogenides (TMDs) have emerged as representative quasi two dimensional (2D) materials with unique physical and chemical properties which are useful for device applications [1-3]. Recently, $MoSe_2$ in particular, has attracted a considerable attention in various fields such as optoelectronics, batteries etc. [1, 4].

In principle, 2D monolayer can be rolled in the form of nanotubes. Few transition metal dichalcogenides nanotubes (TMDNTs) have already been synthesized experimentally [5] and being studied computationally [6]. However, less attention has been paid to tune the electronic and the thermoelectric performance of $MoSe_2$ nanotubes. A recent study [7] suggests that the thermoelectric efficiency of TMDs nanotubes is quite low as compared to their monolayer counterpart. Therefore, in the present work we explore the Lithium intercalation as a route to enhance the electronic and thermoelectric properties of armchair (6, 6) and zigzag (10, 0) $MoSe_2$ nanotube.

COMPUTATIONAL DETAILS

In this work, we have performed first principles calculations within the framework of Density Functional Theory (DFT) using SIESTA program package [8, 9]. A GGA-PBE functional has been used to approximate exchange correlation energy. A supercell of 1x1x3 and 1x1x2 has been used to model armchair (6, 6) and zigzag (10, 0) nanotube of $MoSe_2$, respectively. The vacuum region of ~ 40 Å along x and y direction has been introduced to avoid the interactions between periodic images of nanotube. A 200 Ry mesh cutoff has been used for the reciprocal space expansion of the total charge density. Brillion zone has been sampled by using 1×1×15 Monkhorst-Pack of k-points. Electrical and thermoelectric parameters namely; Seebeck coefficient (S), electrical conductance (G_0), electronic thermal conductance (K_e) has been obtained using GOLLUM code [10]. GOLLUM takes the Hamiltonian matrix (obtained from converged SIESTA runs) as input and calculates s-matrix and associated thermoelectric quantities.

RESULTS AND DISCUSSION

Structural and Electronic Properties

Our study begins with investigation of structural and electronic properties of pristine $MoSe_2$ nanotube. The lattice constant of 3.36 Å and 5.34 Å has been found for armchair (6, 6) and zigzag (10, 0) nanotube, respectively. Optimized structure of both armchair and zigzag nanotube has been presented in figure 1 along with electronic band structure. The armchair nanotube

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is an indirect narrow band gap semiconductor while zigzag naotube is a direct band semiconductor with calculated band gap of 0.04 eV and 0.10 eV, respectively, which is in agreement with the previously reported values [7]. The atom projected electronic density of states depicts that the major contribution at valance band maxima (VBM) and conduction band minima (CBM) originates from Mo atoms.

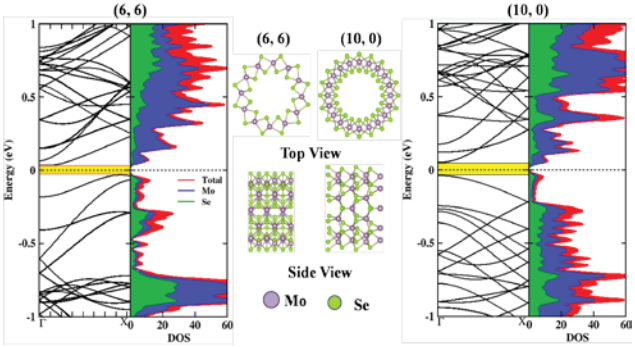

FIGURE 1. Plot of electronic band structure and atom projected density of states for pristine armchair (6, 6) and zigzag (10, 0) $MoSe_2$ nanotube with corresponding ball and stick model showing top and side view.

To find the stability of Lithium inside nanotubes; the binding energy (E_b) has been calculated as

$$E_b = E_{Li+MoSe_2} - E_{MoSe_2} - E_{Li} \qquad (1)$$

Where $E_{Li+MoSe_2}$ is total energy of composite system, E_{MoSe_2} and E_{Li} is the total energy of $MoSe_2$ nanotube and isolated Li atom respectively. Note that Li intercalated nanotubes were fully relaxed to obtain the equilibrium configurations.

In the equilibrium configuration, Li atom is located at the centre of the tube. It has binding energy of -1.27 and -1.31 eV in the armchair (6, 6) and zigzag (10, 0) $MoSe_2$ nanotube, respectively.

TABLE 1. Li intercalated $MoSe_2$ nanotubes: Diameter of nanotube; d, Li-Se distance; $R_{Li\text{-}Se}$, binding Energy; E_b.

Chirality	d (Å)	$R_{Li\text{-}Se}$ (Å)	E_b (eV)
(6, 6)	9.29	4.64	-1.27
(10, 0)	9.44	4.71	-1.31

Li intercalation leads to modification in the electronic structure of pristine $MoSe_2$ nanotubes. It can be seen from figure 2 that the conduction band overlaps with the valance band leading to semiconductor-metal transition upon Li intercalation. Two bands from the conduction band crossed the Fermi level in the armchair (6, 6) $MoSe_2$ nanotube while one band crosses the Fermi level in the zigzag (10, 0) $MoSe_2$, indicating $2G_0$ and $1G_0$ ballistic conductance, respectively. The atom projected density of states reveal that the shift of the energy bands in the vicinity of the Fermi level is due to downward movement of Mo states.

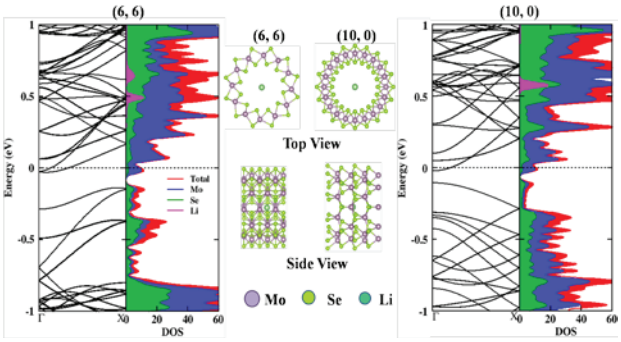

FIGURE 2. Calculated electronic band structure and atom projected density of states for Li intercalated armchair (6, 6) and zigzag (10, 0) $MoSe_2$ nanotube with corresponding ball and stick model showing top and side view.

Thermoelectric Properties

Next, we investigate the thermoelectric performance of pristine and intercalated $MoSe_2$ nanotubes of (6, 6) and (10, 0) chirality. A good thermoelectric material must essentially be able to convert dissipating heat into electrical energy. The modulation in electronic properties of pristine $MoSe_2$ nanotubes with Lithium intercalation is pointing to an expected influence on thermoelectric performance of $MoSe_2$ nanotubes under investigations. The efficiency of thermoelectric materials and devices is determined by their thermoelectric figure of merit (ZT) which has been calculated as

$$ZT_e = \frac{S^2 G T}{K_e} \qquad (2)$$

where, S is the Seebeck coefficient, G is electrical conductance, T is temperature and K_e is electrical thermal conductance. Figure 3 depicts calculated temperature dependent electrical and thermal conductance (G, K_e), seebeck coefficient (S), Power factor (PF) and figure of merit (ZT_e) for pristine and Li intercalated (6, 6) and (10, 0) nanotubes of $MoSe_2$. A large value of S is predicted for pristine armchair (6, 6) $MoSe_2$ naotube as compared to zigzag (10, 0) $MoSe_2$ nanotube, though the electrical thermal conductance (K_e) is larger for the (10, 0) chirality relative to that of the (6, 6) chirality.

Furthermore, in the case of intercalated armchair (6, 6) $MoSe_2$, thermal conductance increases as compared to the pristine nanotube that result in lowering of Power Factor (PF) and hence the ZT_e. In case of (10, 0) nanotube high magnitude of the

Seebeck coefficient and low thermal conductance leads to increase in power factor and hence ZT_e. The modulation in S can be attributed to the observed asymmetry of DOS in the vicinity of Fermi energy (see figures 1 & 2).

The room temperature ZT_e for the pristine and intercalated $MoSe_2$ nanotubes is tabulated in table 2. As compared to pristine nanotubes; Lithium intercalation reduces the ZT_e from 2.13 to 0.30 in armchair (6, 6) $MoSe_2$ nanotube while ZT_e increases from 0.31 to 1.68 for zigzag (10, 0) $MoSe_2$ nanotube. In a recent study [7], the maximum room temperature ZT of armchair (6, 6) and zigzag (10, 0) $MoSe_2$ nanotube was found in the range of 0.2-0.35 which is much lower than our calculated values. Note that here phonon thermal conductance has not been included to calculate ZT which could be the cause of higher ZT in our case. However, our result suggests that Li intercalations influence the DOS near Fermi energy of $MoSe_2$ which essentially results in higher ZT_e in $MoSe_2$ nanotube.

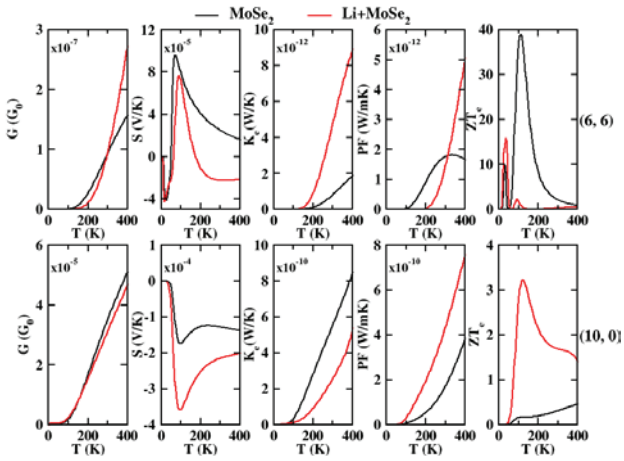

FIGURE 3. Calculated temperature dependent electrical and thermal conductance (G, K_e), seebeck coefficient (S), Power factor (PF) and figure of merit (ZT_e) for pristine and Li intercalated armchair (6, 6) and zigzag (10, 0) $MoSe_2$ naotube.

TABLE 2. Room temperature (@300K) electrical and thermal conductance (G, K_e), Seebeck coefficient (S), Power factor (PF) and figure of merit (ZT_e) for pristine and Li intercalated (6, 6) and (10, 0) nanotubes of $MoSe_2$.

Chirality	System	G (G_0)	S (V/K)	K_e (W/K)	PF (W/mK)	ZT_e
(6, 6)	$MoSe_2$	0.94E-07	2.50E-05	0.82E-12	1.76E-12	2.13
	Li+$MoSe_2$	0.95E-07	-2.25E-05	4.80E-12	1.44E-12	0.30
(10, 0)	$MoSe_2$	3.52E-05	-1.27E-04	5.57E-10	1.72E-10	0.31
	Li+$MoSe_2$	3.12E-05	-2.15E-04	2.57E-10	4.34E-10	1.68

CONCLUSIONS

In this work, we have carried out first principles calculations to investigate the electronic and thermoelectric properties of pristine and Li intercalated $MoSe_2$ nanotubes of (6, 6) and (10, 0) chirality. The pristine zigzag (10, 0) $MoSe_2$ is direct band gap semiconductor while armchair (6, 6) $MoSe_2$ have indirect narrow band gap. A semiconductor to metallic transition takes place with Li intercalation. A maximum room temperature ZT_e of 2.13 and 1.68 are calculated for pristine armchair (6, 6) $MoSe_2$ and intercalated zigzag (10, 0) $MoSe_2$ nanotubes, respectively. The enhancement in calculated ZT_e is attributed to the higher magnitude of Seebeck originating from the asymmetry of DOS in the vicinity of Fermi energy. Thus, our study suggests that $MoSe_2$ nanotube of zigzag chirality could prove to be an efficient thermoelectric material for device application.

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