Ab initio study of MgTe self-interstitial (Mg_i and Te_i), a wide band gap semiconductor

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Abstract. We present results of the formation energy and charge state thermodynamic transition levels of Mg and Te interstitials in MgTe wurzite structure. We use the generalized gradient approximation (GGA) and local density approximation (LDA) functionals in the framework of density functional theory (DFT) for all calculation. The formation energies of the Mg and Te interstitials in MgTe for both the tetrahedral and hexagonal configurations using the different functionals were calculated. The Mg and Te interstitials in MgTe depending on the functional, introduced transition state levels that are either donor or acceptor within the band gap. The Te interstitial exhibit charge states controlled metastability, negative-U and DX centre properties. The Mg interstitial acts as both deep or shallow donor and there is no evidence of acceptor levels found for the Mg interstitial.

Introduction

The semiconductor materials of magnesium and group VI (Se, Te) elements have been attracting attention in recent years due to their wide and direct band gap [1]. They are used in various commercial applications in electronics [1], solid state laser devices, photo detectors [1], and low dielectric constant luminescent devices[1]. Several authors have investigated the MgTe electronic, structural and phonon properties [2, 3, 4]. Intentional doping of MgTe serves as an avenue to introduce charge carriers, which would lead to the modification of its electronic properties. Several authors [5] have reported the presence of donor-complex (DX) and acceptor-complex (AX) centre in MgTe. Chadi *et al.* [5] showed that the localized donor state in MgTe is similar to those arising from DX centre in AlGaAs alloys. It has been shown that the properties of impurities in MgTe are similar to those in ZnTe and their ternary MgCdTe alloys [1, 5]. This similarity has been exploited by doping MgTe with Zn as potential candidate to complement existing CdTe and $Cu(In,Ga)Se_2$ solar materials [6], where a large band gap is essential. To the best of our knowledge, results of electrical activities of the Mg and Te interstitials (Mg_i, Te_i) in MgTe (wurzite (WZ) structure) is lacking. In this work, we present density functional theory (DFT) calculation of the electronic properties of Mg_i and Te_i (hexagonal (H) and tetrahedral (T) configurations) interstitial in the WZ structure of MgTe. The most stable configuration, thermodynamic transition levels and formation energies are presented.

Methodology

DFT electronic structure calculations were performed using the Vienna *Ab initio* Simulation Package (VASP) [7]. The projector-augmented wave (PAW) used to describe the electron wave functions [7]. The calculations were carried out using the LDAand generalized gradient approximations (GGA-(PBE, PBEsol)), to describe the exchange-correlation functional. For the bulk

system, geometric optimization of MgTe structure as well as the band structure calculations were performed in the unit cell using an 8^3 Monkhorst-Pack k-point Brillouin zone sampling scheme and cutoff energy of 400 eV. For the pristine, we employed 128-atom supercells using a 2^3 Monkhorst-Pack k-points Brillouin zone-sampling scheme and cutoff energy of 400 eV. Spin orbit coupling was taken into account in all the calculations. To calculate the defect formation energy and charge states transition energy ($\epsilon(q/q')$) levels, we calculated the total energy $E(d,q)$ for a supercell containing the optimized defect d in its charge state q. The defect formation energy $E^f(d,q)$ as a function of electron Fermi energy (ε_F) was calculated according to Refs. [8, 9]. The defect transition energy level $\epsilon(q/q')$ is the Fermi energy, which the formation energy of charge state q equals that of charge state q' is calculated based on Refs [9, 10].

Results and Discussion

Properties and energetics of Te_i and Mg_i

For the optimized Te_i self interstitials, two competing geometric interstitial structures are considered; namely the tetrahedral (T) and hexagonal (H) configurations both lying in the $100-plane$. For the Te_i, defect atom is bonded to the nearest Mg atoms with three and six fold coordinates for T and H configurations, respectively. For both the T and H configurations, the defect atom bond length with the nearest neighbour Mg atom is 2.82 Å, which is 0.22Å less than the bulk Mg and Te bond length. Interestingly, all the functionals predicted approximately the same bond length. For the optimized Mg_i self interstitial, two competing geometric interstitial structures are considered, namely; the T and H configurations both lying in the $100-plane$. For the H and T configurations, the defect atom forms bond length of 2.98 Å with Te which is 0.04 Å less than the bulk. Similar to the Te_i, the various functionals considered predicted approximately the same bond length.

Table 1: The formation energies (E^f) in eV at $\epsilon_f = 0$ of various charge states for H and T configurations of Te_i in MgTe using LDA PBE and PBEsol. The configurations with the lowest charge states in bold describing the charge states metastability.

Types	Configuration	Charge states				
		−2	−1	0	1	2
LDA	H	**4.50**	**1.67**	**-1.02**	**-1.35**	**-1.26**
	T	4.83	1.90	1.15	0.40	-0.53
PBE	H	**5.54**	**2.60**	**-0.08**	-0.53	-0.36
	T	5.91	2.80	-0.06	**-0.76**	**-1.17**
PBEsol	H	8.07	2.22	**0.05**	**-0.54**	**-1.46**
	T	**4.68**	**2.08**	0.65	0.84	-1.13

Te interstitial (Te_i) in MgTe

Table 1 lists the formation energies in eV of the −2, −1, 0, +1 and +2 charge states for the H and T configurations. All functionals predicted that the formation energies of H increase from double positive to double negative charge states. This same trend is observed for the T configurations. While LDA predicts the lowest formation energy for the H configuration, PBE predicts the lowest formation energy in all charge states for the T configurations. In both the H and T configurations, the formation energies are low suggesting the ability of Te_i to form under equilibrium condition. One important interesting finding is the charged state controlled metastability as predicted by the PBE and PBEsol. The charge states metastability indicates that, even though the T and H configurations of the Te_i defect have the same number and

type of atoms, the stability of T over H configuration is charge-state dependent. Table 2 lists

Table 2: The charge state transition levels $\epsilon(q/q')$ above E_V (eV) for H and T configurations of Te interstitial in MgTe using LDA, PBE and PBEsol.

		$(+2/+1)$	$(+1/0)$	$(0/-1)$	$(-1/-2)$	$(+2/-1)$	$(+2/0)$
LDA	H	-	0.33	-	-	-	-
	T	-	-	-	-	0.81	-
PBE	H	-	0.45	2.67	-	-	-
	T	0.21	0.69	-	-	-	-
PBEsol	H	0.94	1.04	1.72	-	-	-
	T	-	-	1.45	2.61	-	0.89

the calculated transition state energy levels $\epsilon(q/q')$ as a function of the the Fermi energy with reference to the VBM. For the H configuration, deep levels are predicted by all the functionals, these deep levels are either close to the middle of the band gap as in the case of PBEsol or about 0.3 and 0.45 eV away from the the VBM as predicted by PBE and LDA, respectively. While PBE and PBEsol predicted both single acceptor and donor levels, LDA predicted only a single donor level at $\epsilon(+1/0)$. In addition to the single donor, is the double donor $\epsilon(+2/+1)$ as predicted by PBEsol. For the T configuration, we observed both shallow and deep levels as predicted by both the PBE and PBEsol. The $\epsilon(0/-1)$ transition level as predicted by PBE is lying close to the conduction band minimum (CBM), this is in contrast to the prediction of PBEsol, which same level is in the middle of the band gap. But remarkably, according to the prediction of PBEsol, we found the $\epsilon(-1/-2)$ transition level lying close to the CBM. Another interesting transition level predicted by PBE that is absent in other functional is the double ionized states of $\epsilon(+2/+1)$ which is about 0.2 eV above the VBM. In contrast to PBE and PBEsol, LDA functional did not predict any acceptor level. While in the T, Te_i is predicted to acts as a double donor by PBE, PBEsol predicts Te_i as a double acceptor. The mid-gap transition levels of Te_i in the MgTe reveals the properties of deep donor level leading to a DX centre. This centre created by large lattice distortion give rise to the displacement of impurity or host atom, and also leads to the self compensation of a shallow donor through the formation of an acceptor state. A *negative*$-U$ defect occurs when an ionized defect captures two electrons with the second electron being more tightly bound than the first. This probably results from lattice relaxations and gives rise to metastability. LDA predicted a transition level of $\epsilon(+2/-1)$, exhibiting the $negative - U$ behaviour with $effective - U$ value of 0.18 eV. In this predicted $negative - U$ system, we found that the q = +1 and q = 0 charge states are unstable with respect to dissociating into q= +2 and q = −1 states.

Table 3: The formation energies E^f in eV at $\epsilon_f = 0$ of various charge states for T and H configurations of Mg_i in MgTe using LDA and GGA.

Types	Configuration	Charge states				
		-2	-1	0	$+1$	$+2$
LDA	H	8.72	5.76	2.97	0.74	-0.97
	T	10.97	7.71	4.65	1.88	-0.41
PBE	H	9.27	6.17	3.22	1.00	-0.70
	T	8.88	5.60	6.78	-0.40	-1.70
PBEsol	H	7.90	5.26	2.79	-0.77	-0.79
	T	18.52	15.14	3.10	9.11	6.78

Mg interstitial (Mg_i) in MgTe

Table 3 lists the calculated formation energies of charges of Mg_i for T and H configurations. As is observed for the Te interstitial in MgTe for both the T and H configuration, the formation energy increases from double positive to double negative charge states. The PBE predicted the T configuration to be more energetically stable than the H configuration, except in the neutral charge state of H which the formation energy was lower than the neutral charge state of T. In both configurations, as predicted by the three functionals, the formation energy of Mg_i is low, suggesting that this defect can form under normal equilibrium condition. But in general, the formation energy of the Te_i is lower than that of Mg_i. This is in agreement with recent report by Ji *et al* [12].

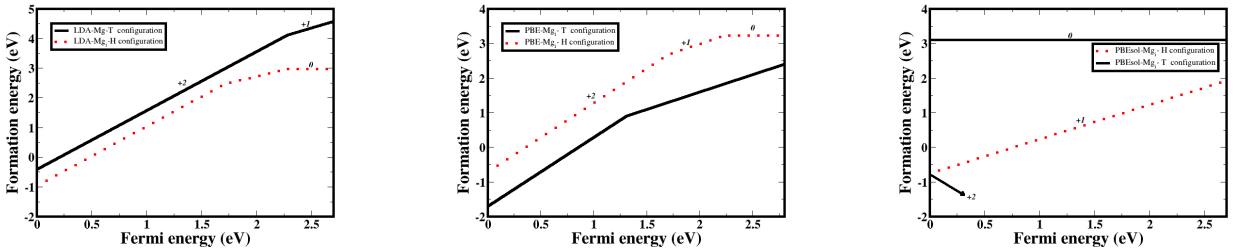

Fig. 1: Plot of formation energies as a function of the Fermi energy for Mg_i in MgTe using (left) LDA; (centre) PBE and (right) PBEsol.

The plot of the formation energy as function of Fermi energy as predicted by the LDA, PBE and PBEsol are displayed in Fig.1, where the slope of the energy line gives the charge state of a defect and the inflexions are the calculated transition energy levels. In the H configuration, the LDA and PBE, predicted transition level with energy of 2.30 eV for the $\epsilon(+1/0)$. For the T configuration, the PBEsol (see Fig.1 (right)) did not predict any charge state transition level. This is in contrast to Te_i where for the T configuration, charge state transition levels are predicted. For the T configuration as shown in Fig.1 (left), the LDA predicted a donor level of $\epsilon(+2/+1)$ at E_V + 2.28 eV. This same double ionized state is also predicted by PBE at 1.31 eV above the VBM lying at the middle of the band gap. For the H configuration, the LDA, PBE and PBEsol predicted 1.7, 1.70 and 0.03 eV for the $\epsilon(+2/+1)$ transition level. In addition, the LDA and PBE predicted both double donor levels almost at the middle of the band gap, in contrast to LDA and PBE, PBEsol predicted a shallow donor level lying close to the VBM at E_V +0.03 eV. While the charge state transition levels in the H configuration are above the thermodynamically stable region of the T configuration as predicted by PBE (see Fig.1 (centre)), the reverse order is predicted by both LDA and PBEsol. In Mg_i, there is no prediction of $negative - U$ as it is for the case of Te_i by LDA.

Summary

The formation of the Mg_i and Te_i in both the H and T configurations are energetically stable under equilibrium condition. The defect Te_i with a more valence electron is more stable than the defect Mg_i which has less valence electron. For the Te_i, we observed donor and acceptor levels as predicted by all the functionals. While the PBEsol predicted double acceptor level at $(-1/-2)$, the PBE predicted double donor level at $(+2/+1)$ and LDA predicted $negative - U$ properties at $\epsilon(+2/-1)$. For the H configuration of Te_i, we found a single donor level far away from VBM as predicted by all the functionals. In addition PBEsol predicted a single acceptor level at the middle of the band gap. All the functionals predicted that the Mg_i induced charge state transition levels in the band gap that behaves as double and single donor. According to

PBEsol, for the H configuration, the double donor transition state is shallow lying 0.03 eV away from the VBM while in the T configuration there is no level predicted. For both configurations, LDA and PBE predicted a deep double donor level lying close to the middle of the band gap.

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Table 4: Author's background

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