The electronic and optical properties of monovalent atom-doped ZnO monolayers: the density functional theory

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Abstract. The current study deals with the structural, electronic and optical properties of monovalent element-doped ZnO monolayers using density functional theory. Specifically, we have considered structural and optical properties of monovalent ($M = \text{Li, Na and K}$) atom-doped ZnO monolayers. Among these monovalent elements, the substitution of Li with Zn atom maintains the hexagonal planar geometry of the ZnO monolayer, but Na and K elements protrude out from the plane of the ZnO monolayer. The Li atom binds more strongly with the ZnO sheet compared with Na and K atoms. A Li-doped ZnO monolayer shows metallic behaviour whereas Na- and K-doped ZnO monolayers show half metallic magnetic behaviour. The magnetic moment is of the order of $1\mu_B$. The magnetic moment mainly originates from nonbonding O_p states. The substitution of an alkali metal element-doped ZnO monolayer leads to a red-shift in optical spectra. The dielectric constant of a monovalent element-doped ZnO sheet increases compared with that of a pristine ZnO sheet. This study provides the basis to develop opto-electronic devices using doped ZnO monolayers.

Keywords. ZnO monolayer; density functional study; optical properties.

1. Introduction

ZnO has emerged as a promising semiconductor material for modern technological applications because of its particular electric and optical properties. Owing to its large direct band gap (3.4 eV) and exciton binding energy (60 meV) [1], the compound is suggested as a material for opto-electronic devices, such as light emitting diodes, lasers, etc. [2,3]. Moreover, its piezoelectric and pyroelectric properties make ZnO a promising candidate for sensors, actuators and energy generators [4]. ZnO is also suggested for spintronics and in other application areas in science such as biotechnology and in medical applications [2,5]. Until now, most of the existing research focused on bulk ZnO and thin films of ZnO [1,6]. Several interesting nanostructures of ZnO such as nanotubes, nanowires, nanorods, nanoribbons, nanoflowers and nanosheets [2,4,7,8] have been reported. Recently, two-dimensional (2D) structures of ZnO have been attracting increasing research interest due to their some special features such as high surface to volume ratio, nanometre scale thickness and promising optical and photocatalytic activities. Monolayer-thick ZnO (0001) films were successfully synthesized using Zn and O atoms being arranged in planar sheet-like in a hexagonal boron-nitride prototype structure [7–9], expanding the family of 2D materials. Very recently, *in situ* observations of free-standing graphene-like monolayer and bilayer ZnO have been reported [10]. These experimental pieces of evidence provide a platform to design ZnO monolayer-based new opto-electronic devices.

Tuning the electronic properties specifically of a band structure is of great importance in designing semiconductor devices and it can be simulated by doping. As impurity atoms are introduced, the spatial geometries which provide the lowest energy configuration in the bulk may not provide the same when the surface atoms and surface bonds are altered. Such modifications are much more important in many electronic and opto-electronic devices, especially in injection lasers and bipolar transistors [3,4]. Doping of ZnO nanostructure with metal ions is a strategy to modify their electronic and optical properties and improve their applications in miniaturized opto-electronics devices [4]. There are a few reported studies regarding the optical properties of ZnO monolayers [11–16]. Mg doping in the ZnO monolayer and higher concentrations of Al and Ga element-doped ZnO monolayer lead to a blue-shift of the optical absorption peaks [11,12], while N, Cu, Be, In and Cd doping is found to result in a red-shift of the absorption peaks [13–16]. As is known, alkali metals have good electrical and thermal conductivities, however, the doping of monolayer with these metals has been rarely discussed [17,18]. The first-principles study has shown that Sn-doping (n-type) and Li-doping (p-type) in a ZnO nanosheet have high stability compared with Li–Ni codoping in a ZnO nanosheet [18]. This study suggested that a ZnO nanosheet may be used as an alternative functional material as a p–n homo-junction. In view of the novel 2D character of the ZnO monolayer, Fang *et al* [17] have explored the magnetic properties of a K-doped ZnO monolayer using density functional theory (DFT). A comparative study of different effects of alkali elements

on structural and optical properties of ZnO monolayer can lead to better understanding of these materials as acceptors in ZnO structures. Such knowledge can enhance development of ZnO nanostructure-based opto-electronic devices. In the current study, using DFT, we have investigated the doping effects of alkali (Li, Na and K) elements on the structural, electronic and optical properties of a ZnO monolayer. In section 2, we describe in brief the computational details, followed by discussion of our results in section 3. In section 4, conclusions are given.

2. Computational details

All the computations have been performed using spin-polarized DFT using the VASP code [19]. The ionic potentials are represented by Projector Augmented Wave potentials [20–22]. The exchange correlation energy is represented by a generalized gradient approximation (GGA) functional proposed by Perdew, Burke and Ernzerhof (PBE) [23]. The wave functions are expressed in a plane wave basis set with an energy cutoff of 400 eV and Brillouin zone integration was performed using a $5 \times 5 \times 1$ k -point mesh within the Monkhorst scheme. We have considered the 4×4 supercell of a ZnO monolayer with 16 Zn and 16 O atoms. During the periodic calculations, a vacuum space of 15 Å has been inserted along the z direction to minimize the interaction between the ZnO sheets. The configuration of doped ZnO sheet is optimized until the forces on all atoms are <0.01 eV Å⁻¹ and with the energy convergence of 10^{-5} eV. To understand the electronic structure, we have calculated band structure, density of states (DOS) and work function.

The optimized configurations are further used to calculate the optical properties. The frequency-dependent dielectric matrix is calculated using VASP 5.2 optical programs [19]. For the electronic structure calculations, the Brillouin zone for the 4×4 supercell is sampled by $11 \times 11 \times 1$ k -point. The frequency-dependent dielectric matrix calculations are carried out by increasing the number of states by a factor of 3. The real and imaginary dielectric values of the materials are plotted for all photon energies. From the real part of dielectric function, dielectric constant is calculated and absorption spectra are obtained from the imaginary part of the dielectric function.

3. Results and discussion

First, the structure of a pure ZnO monolayer is presented to examine the reliability of the DFT/GGA calculations in figure 1a. The calculated Zn–O bond length in the ZnO monolayer is 1.89 Å which is lower than the bulk ZnO bond length (2.01 Å). The Zn–O–Zn or O–Zn–O bond angle is 120°. To understand the electronic structure, we have calculated band structure and DOS of ZnO monolayer (figure 1b). The spin-polarized calculations showed that the ZnO monolayer is a

Figure 1. (a) The geometric structure of ZnO monolayer. Pink and red colour atoms represent the zinc and oxygen, respectively. The numbers represent Zn–O bond length (Å) and bond angle O–Zn–O (°). (b) The calculated band structure along with total DOS of ZnO monolayer. The number in the band structure indicates the band gap (eV) of pristine ZnO monolayer. The labels on total DOS indicate contribution from dominant states. Fermi level (horizontal dashed line) is aligned to 0 eV. (c) The total charge density of ZnO sheet at 1/5th of its maximum value. The numbers represent the Bader charge on Zn and O atoms.

nonmagnetic semiconductor. The calculated band structure indicates that the ZnO monolayer exhibits a direct band gap at the Γ point with an energy gap of 1.66 eV. It is known that the GGA-PBE method generally underestimates the band gap [24]. From the total DOS, it can be seen that the valence band near the Fermi level is dominated by O_{2p} with a small contribution of Zn_{3d} states and the conduction band is mainly contributed with O_{2p} and Zn_{4s} states. Figure 1c presents the total charge density along with the Bader charge on Zn and O atoms. From the Bader charge analysis [25], the charges on Zn and O atoms are +1.18e and –1.18e, respectively. The localized charge density on Zn and O atoms clearly shows the ionic nature of the ZnO monolayer. All the results are consistent with the earlier studies [10,17,24]. This also further indicates the accuracy and reliability of the modelling element used to calculate the optical properties of a monovalent-doped ZnO monolayer.

Now the structural properties and stability of alkali metal atom-doped ZnO are presented. The structures of alkali metal atom (M = Li, Na and K)-doped ZnO monolayer are optimized by considering spin-polarized calculations. Initially, we considered both the substitutional sites, Zn as well as O for the dopant (M) atom. The formation energy of the alkali element atom-doped ZnO monolayers is calculated, for understanding of its relative stability. The formation energy (E_{form}) can be defined as:

$$E_{\text{form}} = E[\text{M} : \text{ZnO}] - E[\text{ZnO}] + \mu[\text{Zn}] - \mu[\text{M}], \quad (1)$$

where $E[M : \text{ZnO}]$ is the total energy per atom of the M-doped ZnO sheet, $E[\text{ZnO}]$ is the total energy per atom of a pure ZnO sheet, $\mu[\text{Zn}]$ and $\mu[\text{M}]$ represent the chemical potentials of Zn and M atoms [26], respectively. The formation energies for Li-, Na- and K-doped ZnO monolayers are -2.28 , -2.00 and -2.23 eV, respectively where M atom is doped at the Zn site. The formation energies of M@ZnO where M atom is doped at the O site are -2.03 , -1.71 and -1.84 eV for the Li-, Na- and K-doped ZnO monolayer, respectively. For all the systems, the formation energy is found to be negative indicating the exothermic nature of the doping process. The more negative value of the formation energy is found with the substitution of M dopant at the Zn site compared with that of substitution of M at the O site. This indicates that the substitution of Zn atom with alkali metal atoms is more favourable compared with that of O site in the ZnO monolayer. Among all three elements, more negative value of formation energy for the Li-doped system shows that the doping of Li in the ZnO sheet is more favourable compared with that of Na- and K-doped systems. In the rest of the discussion, we have kept our focus on the M@Zn in the ZnO monolayer where the M atom substitutes the Zn atom.

Figure 2. Optimized configuration of Li-, Na- and K-doped ZnO sheet along with M–O and Zn–O bond lengths (Å) and bond angle O–M–O (°). Front and side views are shown for each configuration. The label on the side view with H_z represents the height of dopant atom along the z -axis from the ZnO sheet (Å). Pink and red colours represent the zinc and oxygen atoms, respectively. Blue colour represents doped monovalent element M (M = Li, Na and K).

Figure 2 presents the optimized configurations of Li-, Na- and K-doped ZnO monolayer (M@ZnO). The structural parameters for monovalent-doped systems are summarized in table 1. The ionic radii of Zn, Li, Na and K atoms are 0.83, 0.78, 0.98 and 1.33 Å, respectively. The effects of size are dominantly observed with the substitution of M at the Zn site. The side view of figure 2 shows that the small size Li atom remains in the plane of the ZnO monolayer while Na and K move outwards from the sheet. Among Li, Na and K atoms, the substitution of Zn by Li atom with slight distortion maintains the 2D hexagonal planar geometry of the ZnO monolayer. Li–O bond lengths are around 1.87 Å. In the presence of Li, the Zn–O bond lengths decrease from 1.89 to 1.86 Å. The doping of relatively large size Na or K atom at the Zn site induces significant distortion in the ZnO monolayer. After relaxation, it is found that the Na/K atom protrudes from the plane of the monolayer. The distance of Na atom from the ZnO sheet along the z -axis is 0.85 Å. In the Na-doped ZnO monolayer, the Na–O distance is 2.15 Å and O–Na–O angle is 110.6°. The large size Na atom creates strain on the nearest Zn–O bonds. The Zn–O bond lengths in the Na-doped ZnO sheet decrease from 1.89 to 1.85 Å. Similar to Na, the K atom prefers to come out of the plane of the ZnO monolayer. The distance of K atom from the ZnO sheet along the z -axis is 1.40 Å. With the increase in the ionic radius of M atom, the distance of M atom from the plane of the ZnO monolayer increases. The K–O distance is 2.55 Å and O–K–O angle is 87.6°. The Zn–O bond length decreases from 1.89 to 1.83 Å compared with that of pristine ZnO monolayer. The large distance of K atom from the ZnO monolayer along the z -axis shows the weak interaction with the ZnO monolayer.

Table 2 presents the charge transferred from M atom to the nearest three O atoms. The charge transfer from Li to the nearest O atoms is $+0.88e$. In case of Na-doped ZnO monolayer, the charge transfer increases slightly to $+0.89e$. It is seen that increase in the distance of K atom from the ZnO monolayer along the z -axis reduces the charge transfer from K to the nearest O atoms. The charge transfer from K to the nearest O atoms is $+0.84e$, which is smaller compared with that of charge transfer from Li and Na to the nearest three O atoms. The K–O bonds are longer compared with the Li–O and Na–O bonds, showing the weak interaction of K with the

Table 1. The structural parameters of M@ZnO along with the pristine ZnO sheet with average bond lengths of Zn–O and M–O (Å), bond angle (°), height H_z of dopant atom along the z -axis from the ZnO sheet (Å) and formation energy E_{form} (eV), where M = Li, Na and K.

System	Bond length (Å)		Bond angle (°)		H_z (Å)	E_{form} (eV)
	Zn–O	M–O	$\theta_{\text{O–Zn–O}}$	$\theta_{\text{O–M–O}}$		
ZnO monolayer	1.89	—	120	—	—	—
Li@ZnO	1.86	1.87	122.9	120.2	0	-2.28
Na@ZnO	1.85	2.15	125.2	110.6	0.85	-2.00
K@ZnO	1.83	2.55	125.9	87.6	1.40	-2.23

Table 2. Bader charge analysis of M@ZnO sheets along with the pristine ZnO sheet. The charges on the Zn, O and M dopant (M = Li, Na and K) are defined here.

System	Charges on ZnO sheet		Charge on dopant
	Zn	O	M
ZnO sheet	+1.11e to +1.18e	-1.11e to -1.18e	—
Li@ZnO	+1.15e to +1.19e	-1.15e to -1.20e	+0.88e
Na@ZnO	+1.11e to +1.21e	-1.09e to -1.19e	+0.89e
K@ZnO	+1.11e to +1.21e	-1.12e to -1.19e	+0.84e

ZnO monolayer. The large size K induces more defects in the ZnO monolayer. In the presence of Na/K, the charge transfer from Zn to O increases compared with the charge transfer in the ZnO monolayer. Our spin-polarized calculations show that the Li-doped ZnO monolayer prefers the nonmagnetic state while Na@ZnO and K@ZnO show magnetic behaviour. The Na/K dopant induces a total magnetic moment of $1\mu_B$. Using DFT, Fang *et al* [17] have studied the magnetism in the K-doped ZnO monolayer. They found that the substitution of K atom in the ZnO monolayer distorts the host structure significantly with the induced magnetic moment of $1\mu_B$.

It is noted that the pristine ZnO monolayer exhibits semi-conducting behaviour with a direct band gap of 1.66 eV, consistent with earlier reports [10,17,26]. The band structure calculation (not shown) revealed that after doping alkali element atom-doped ZnO monolayers show metallic characteristics. Due to less number of valence electrons of Li, Na and K compared with that of Zn atom, they can be regarded as the p-type dopant in ZnO monolayer. By the substitution of Zn with M atoms (M = Li, Na and K) the top of the valence band crosses the Fermi level and move towards the conduction band. The spin-up and spin-down band gaps for the Li-doped ZnO monolayer are very small nearly 0.11 eV. The Na/K-doped ZnO monolayer shows direct band gap semiconducting behaviour in the spin-up channel but it is important that the spin-down channel is metallic. The impurity bands induced by the Na/K dopant are found above the Fermi level. The spin-up band gaps for Na- and K-doped ZnO monolayers are 1.70 and 1.67 eV, respectively, whereas spin-down band gaps are very small. It results into half-metallic magnetic behaviour for the Na/K-doped ZnO monolayer. The half-metallic characteristic of K-doped ZnO monolayer is consistent with the earlier report [17]. To understand the variation in the band structure and band gap of ZnO monolayer with doping, further we have calculated total DOS and projected DOS on M, Zn and O atoms. Figure 3 shows the total DOS along with the projected DOS of M-doped ZnO monolayer (M = Li, Na and K). The total DOS for the M-doped ZnO sheets show the delocalized nature compared with that of pristine ZnO monolayer. The shifting of the Fermi level to the lower energy is observed with the doping of alkali element in the ZnO monolayer. It is observed that with the substitution of Zn atom by M, the defects in ZnO monolayer increases with the increase in the

ionic radius from Li $\rightarrow$ Na $\rightarrow$ K. From the total DOS, we can see significant variations near the Fermi level. As discussed earlier, in the pristine ZnO monolayer the lower energy part of the spectra is dominated by Zn_{3d} and O_{2p} orbitals. In the M-doped ZnO monolayer from the projected DOS, the contribution of M_{sp} orbital is also observed in the lower energy part of the spectra along with Zn_d and O_p orbitals. It is seen that the hybridization of O_p and M_p bonding states is dominant near the Fermi level with small contribution of M_s . The newly populated energy levels are observed in total DOS of M@ZnO due to the substitution of monovalent M atom. Li interacts more strongly with O atoms compared with that of Zn, results in larger splitting nearer to the Fermi level. Li_p along with $Zn_d + O_p$ are found near the Fermi level. DOS for majority and minority states are symmetric in Li@ZnO suggesting the system to be nonmagnetic. This leads to a semiconductor to nonmagnetic metallic transition. The increase in nonbonding states above the Fermi level shifts the conduction band towards the Fermi energy level. Substitution of Zn atom by Na/K decreases the degree of hybridization leading to the shift of the majority spin near the Fermi level and minority spin above the Fermi level. The major contribution to the magnetic moment is now from the minority spin in Na/K-doped ZnO. The Fermi level passes through the O_p levels for the minority spin, thereby confirming the contribution from the O_p orbitals to the net magnetic moment. The magnetic moment of Na/K-doped ZnO monolayer is $1\mu_B$. To understand the spin polarization, we have calculated the difference charge density. The difference charge density is calculated as the difference between the charge density of M-doped system to the charge density of ZnO monolayer. Figure 4 presents the charge density of doped systems. A careful analysis shows that the spin polarization on O atoms increases from Li $\rightarrow$ Na $\rightarrow$ K. Because of small charge transfer from K to the nearest oxygen atoms and the occurrence of structural deformation, a polarized charge density is observed on the nearest O atoms. In the difference charge density plots, one can see the spin-down (blue colour) charge density on O atoms in the vicinity of the K molecule.

To understand the effects of doping of Li/Na/K atoms on the ZnO monolayer, we have calculated the work function, Φ , of the pristine and M@ZnO sheets. The work function is the minimum amount of energy required to remove an electron

Figure 3. Total DOS and projected DOS of M@ZnO sheet (M = Li, Na and K). Fermi level is aligned to 0 eV (vertical dashed line).

Figure 4. Difference charge densities of the monovalent (M = Li, Na and K) element-doped ZnO sheets. The values in figures represent Bader charge on the Zn, O and M atoms. Red and blue colours indicate spin-up and spin-down charge densities.

from the Fermi level to infinity. The work function can be estimated as

$$\Phi = V(\Phi) - E_f, \quad (2)$$

where Φ , $V(\Phi)$ and E_f are the work function, electrostatic potential at the vacuum level and Fermi energy of the ZnO sheet, respectively. The work function of the

pristine ZnO monolayer is 5.13 eV and it is consistent with earlier calculation [26]. With Li doping the work function increases to 5.42 eV. For Na- and K-doped systems the work function is 5.15 and 4.87 eV, respectively. The decrease in the work function from Li $\rightarrow$ Na $\rightarrow$ K explains the affinity of the ZnO monolayer towards the M atom. This observation is consistent with the variation in M–O bond lengths and Bader charge analysis. The affinity of ZnO monolayer towards the K atom is lower compared with that of Na or Li.

Figure 5. Optical properties of real and imaginary parts along the x and y axis of dielectric function for $M@ZnO$ monolayer ($M = Li, Na$ and K) along with the pristine ZnO monolayer.

Because the band gaps and work functions of the pristine and $M@ZnO$ sheets can effectively be tuned by doping, some effects on the optical absorption of ZnO monolayer are highly expected. The band gap of ZnO sheet is 1.66 eV. The optical band gap of ZnO sheet in the presence of M dopant is calculated between the Fermi level and bottom of the conduction band. The optical band gap of ZnO monolayer increases in the presence of M atom. This shows the p-type semiconducting behaviour of alkali element-doped ZnO monolayer. The optical band gaps for Li-, Na- and K-doped ZnO monolayers are 1.96, 1.92 and 1.73 eV, respectively. These variations in optical band gap affects the optical properties of ZnO monolayer. Finally, we have studied the optical properties of $M@ZnO$ systems in comparison with the pristine ZnO sheet.

The optical properties can be determined from the dielectric function $\epsilon(\omega)$ as a function of frequency and wavelength. As noted earlier, the frequency-dependent dielectric matrix is calculated using VASP 5.2 optical programs [19]. It consist of two parts ϵ_1 and ϵ_2 , which describe the real and imaginary parts of dielectric function, respectively. Figure 5 shows the real and imaginary dielectric functions of pristine and $M@ZnO$ systems along the x and y axis and are plotted for all photon energies. The real part of the dielectric function, ϵ_1 is shown in figure 5. The nature of the curves for the host and $M@ZnO$ systems is nearly the same except for in the lower energy range. From the real part of dielectric function, we have calculated dielectric constant, $\epsilon(0)$. Real part ϵ_1 of dielectric function of ZnO sheet with M dopant along x , y and z is presented in table 3. Here, it is seen that the dielectric

Table 3. Dielectric constant of $M@ZnO$ ($M = Li, Na$ and K) monolayer along with the pristine ZnO monolayer.

System	Dielectric constant		
	ϵ_x	ϵ_y	ϵ_z
ZnO sheet	1.49	1.49	1.18
Li	9.26	7.43	1.18
Na	7.76	4.83	1.19
K	7.38	4.88	1.19

constant of pristine ZnO monolayer is 1.49. It is an isotropic along the x and y directions because of planar geometry [7]. The dielectric constant for the $M@ZnO$ monolayer is found to be higher than that of pristine ZnO monolayer. For Li-, Na- and K-doped ZnO systems the static dielectric constant (ϵ_x) is 9.26, 7.76 and 7.38, respectively. The increase in defect levels from $Li \rightarrow Na \rightarrow K$ restricts the motion of charge carriers and the value of dielectric constant decreases. An anisotropy was found for the dielectric constant of $M@ZnO$ along the x and y directions. The difference in the dielectric constant along the x and y directions increases for the Na/K-doped ZnO monolayer related to the Li-doped ZnO monolayer due to protrude geometry. It is mainly observed in the lower energy range at the defect levels. These variations along the x and y directions are also seen in the imaginary part of dielectric function. The overall decrease in dielectric constant from $Li \rightarrow Na \rightarrow K$ is inversely proportional to the band gap of the doped systems.

From the imaginary part of dielectric function (optical absorption spectra), it is found that M@ZnO has major influence on the optical spectra of the bare system. For the pristine ZnO sheet, the first transition peak is near the band gap energy (~ 1.66 eV) showing direct band gap characteristics. The second transition peak near 7 eV is due to the transition from the lower energy range. These results are similar to the earlier studies [7,11]. A shift in the absorption edge is observed to a lower energy range for M@ZnO compared with that of the host system, which is consistent with the decrease in the band gap of the system. The imaginary part of dielectric function exhibits red-shift behaviour from $\text{Li} \rightarrow \text{Na} \rightarrow \text{K}$. Similar behaviour is observed for the optical characteristics of ZnO nanowires and nanotubes [27–29]. The host system as well as M@ZnO systems show similar behaviour in the range of 2–10 eV. The substitution of Zn with a monovalent atom shows an additional peak in the lower energy range of the spectra for M@ZnO systems (below 1 eV). In this region, the K@ZnO shows a higher absorption intensity peak compared with Li/Na-doped ZnO systems. The shift in optical spectra and addition of a peak in the lower energy range can be related to the defects induced in the ZnO monolayer due to doping of an alkali atom. The lower range absorption spectrum is explained on the basis of local charge mismatch in valency and the size of the M atom. The large structural deformations from $\text{Li} \rightarrow \text{Na} \rightarrow \text{K}$ affect the electronic properties of ZnO monolayer. The enhancement in absorption intensity is understood easily by considering the increasing number of defects or surface states with M doping. It is also due to strain and mismatch in ionic size. The increase in defects enhances the lower energy transitions in the K-doped ZnO monolayer compared with that of Li- and Na-doped sheets.

Overall, it is found that the p-type behaviour of alkali element-doped ZnO monolayer with an increase in optical band gap is similar to thin film studies [30,31]. In case of ZnO nanowires and nanotubes, the red-shift is reported for alkali-doped ZnO nanostructures compared with that of undoped-ZnO nanostructures [27–29]. The variations in the optical properties of alkali-doped ZnO nanostructures are observed due to the dimension effect [27–31]. The possibility of tuning the electronic and optical properties in an alkali element-doped ZnO sheet opens up new opportunities for opto-electronic materials based on oxide semiconductors via band gap engineering. These results will be useful to develop a p-type material with high-dielectric constant using monovalent atom-doped ZnO sheets.

4. Conclusions

The current study performed a comprehensive analysis of the structural, electronic and optical properties of M (M = Li, Na and K) element-doped ZnO monolayer. The results of DFT-based calculations were analysed in terms of energetics, band structure, DOS, work function, absorption spectra

and dielectric constant. The substitution of Li with a Zn atom maintains hexagonal planar geometry but Na and K elements protrude out from the plane of ZnO monolayer. Li binds more strongly by showing metallic behaviour. As the size of the dopant increases strain is induced in the ZnO monolayer with a change from metallic to half-metallic behaviour. Our spin-polarized calculations show that Li-doped ZnO monolayer prefers the nonmagnetic state while Na@ZnO and K@ZnO show the magnetic behaviour. The optical spectra of M@ZnO show a red-shift in absorption spectra of pristine ZnO monolayer. With the doping of alkali elements, the dielectric constant of ZnO monolayer increases. This study can be useful to develop high-dielectric material for opto-electronic devices using alkali element-doped ZnO monolayers.

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