EVALUATION OF TOTAL AND PARTIAL DENSITY OF STATES OF THE PURE EU DOPED WITH ZNO AND THEIR SYSTEMS

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Abstract: Semiconductor metal oxides, with applications in the photoelectrochemical cells, diluted magnetic semiconductors (DMS), field effect transistors, and photoluminescence devices, have recently initiated dynamic research activities [1-3]. In particular, ZnO has a significant advantage for applications in optical [4] and spintronic [5] devices. As a result, doping ZnO with various elements has been a popular technique to manipulate and control ZnO's extrinsic properties for device applications [6]. Specially rare earth (RE)- and transition metal (TM)-doped ZnO systems exhibit interesting optical and magnetic properties, which do not exist in undoped ZnO. Optically, ZnO systems doped with RE ions have been intensively investigated as electroluminors with wide technological applications [7]. In this work, the structural and electronic properties of the ZnO:Eu systems are investigated by a density functional approach. Furthermore, the effects of ZnO's two dominant point defects, Zn interstitial (ZnI) and O vacancy (VO), on the functional properties of these materials are studied. The results of theoretical investigations presented here will shed light on the origin of the functional properties of this relatively new family of materials.

Keywords: DMS, Density Functional approach, Vacancy, RE.

Introduction: Semiconductor metal oxides, with applications in the photo electrochemical cells, diluted magnetic semiconductors (DMS), field effect transistors, and photoluminescence devices, have recently initiated dynamic research activities [1-3]. In particular, ZnO has a significant advantage for applications in optical [4] and spintronic [5] devices. Due to their optical and electrical properties zinc oxide (ZnO) films have been widely studied and have received considerable attention in recent years. ZnO has also gained much attention due to the many advantages over other oxide thin films such as In_2O_3, $CdSnO_4$ or SnO_2. These advantages include non-toxicity, good electrical, optical and piezoelectric behaviors, stability in hydrogen plasma atmosphere and low price. Moreover, ZnO films have many interesting potential applications such as transparent electrode, piezoelectric device, and gas sensor and it can be used as windows layer in heterojunction solar cells (Natsume and Sakata, 2000; Nunes et al., 2001; Paraguay et al., 1999). Pure zinc oxide is an intrinsic semiconductor with high electrical resistivity and a direct band gap of about 3.2eV. As a result, doping ZnO with various elements has been a popular technique to manipulate and control ZnO's extrinsic properties for device applications [6]. Specially rare earth (RE)- and transition metal (TM)-doped ZnO systems exhibit interesting optical and magnetic properties, which do not exist in undoped ZnO. Optically, ZnO systems doped with RE ions have been intensively investigated as electroluminors with wide technological applications [7]. In this work, the structural and electronic properties of the ZnO:Eusystems are investigated by a density functional approach. Furthermore, the effects of ZnO's two dominant point defects, Zn interstitial (ZnI)

and O vacancy (VO), on the functional properties of these materials are studied. The results of theoretical investigations presented here will shed light on the origin of the functional properties of this relatively new family of materials.

RE doped ZnO: An easy way to comply with the in RE doped ZnO, the intraionic 4f transitions of RE ions form luminescent centres which generate narrow and intense emission lines [8]. While the enhancement in the optical absorption of TM-doped ZnO can transfer these materials to efficient photocatalysts [9]. Magnetically, the intrinsic magnetic moment, borne by the RE and TM ions, makes the RE and TM-doped ZnO systems to be potential diluted magnetic semiconductors with applications in spintronic devices. Over the past decade or so, a considerable amount of effort has been made on searching for ZnO-based DMSs with ferromagnetism at ambient. This goal is meant to be achieved by doping ZnO with mainly the first row TMs, such as Co, Mn, and Fe [10]. However, most recently, interesting magnetism has been observed in other metal oxides doped with the second row TMs, namely in Sn2O:Pd system [11]. This stimulated further search for possible ferromagnetism [12] and functional optical properties [13] in ZnO:Pd. The realization of magnetism in the ZnO:Pd system is motivated by a previous theoretical prediction [14] and experimental observation of ferromagnetism in Pd clusters. In addition to systems containing TM ions, Eu-doped ZnO (ZnO:Eu) has also shown room temperature ferromagnetic ordering which is partially caused by the high magnetic moment of the Eu ions.

Method of Findings:

Computational details: Ab initio calculations were performed with a density functional theory-based DMol3 package developed by Accelrys. Geometry optimization and partial density of states (PDOS) calculations were performed with "double-numeric plus polarization" (DNP) basis set while generalized gradient approximation (GGA) based on Perdew-Wang formalism was applied for correlation functional. Real-space global cutoff radii were set for all elements at 5 Å. Since only valence electrons would affect the physical properties, the nuclei and core electrons were replaced by DFT semi-core pseudo potentials with a relativistic correction. A Brillouin zone sampling was carried out by choosing the 2 × 2 × 2 k point set using the Monkhorst Park scheme with a grid spacing of approximately 0.04 -1 Å between k points. The convergence thresholds for energy, Cartesian components of internal forces acting on the ions, and displacement were set to be 10-5 eV/atom, 0.05 eV/Å, and 0.001 Å, respectively. A convergence testing was performed, first by increasing the k point mesh to 3 × 3 × 3; it was found that the total energy differs less by 10-5 eV/atom. Then, the k-point mesh was fixed at 2 × 2 × 2, and the cutoff radii were set for all elements to be 5.5 Å. Once again, no significant change in the total energy was obtained. Thus, the results were well converged. The formation enthalpy and bandgap for undoped ZnO was calculated to be -3.5 and 2.0 eV, respectively. The formation enthalpy is in good agreement with the experimental value of -3.64 eV. However, the bandgap is underestimated by 1.4 eV which is attributed to the GGA intrinsic error. The calculated lattice constants for undoped and fully optimized ZnO were found to be 3.279 Å for a and 5.281 Å for c, which are in good agreement with the experimental data, overestimated by only 0.9% and 1.5%, respectively. The Zn-O bond lengths in the relaxed structure were 2.005 and 1.997 Å along the c direction and ab plane, respectively. In order to avoid the artificial hydrostatic stress in the doped structures, the lattice parameters were fixed to the calculated values of the undoped ZnO while only the internal atomic coordinates were relaxed. To simulate the low concentrations of dopants in ZnO, a large supercell of 4a × 4a × 2c was adopted for calculations. The original supercell contained 64 Zn-O formula units. By introducing one dopant in the substitutional or interstitial site, the concentration of the dopants would be 1.4%. Having the periodic boundary conditions applied, the average separation of the dopant ions is 13.114 Å. This distance is large enough to avoid artificial interaction between the dopants. As a result, the calculations on this supercell will sufficiently resemble the experimental conditions of diluted dopant concentrations. The formation energy (Ef) of the dopants or a cluster of dopants in ZnO's host lattice was calculated as follows:

$Ef = Et(ZnO:M)-Et(ZnO)+n\mu Zn-\mu M+qEF$ (1)

in which Et, μ, and EF represent total energy, chemical potential for respective elements, and Fermi energy, respectively. μZn and μM are set to be the calculated energies of metallic Zn and the dopants (Pd or Eu) per element. n represents the number of Zn atoms removed from the supercell, which is zero in the case of the interstitial dopant and one for the substitutional dopant.q stands for the net number of electrons transferred from the defect to the conduction band. Since only neutral supercells were adapted for the calculations, q is zero for all configurations. The ZnO:Eu system The incorporation mechanism of Eu ions in ZnO's host lattice was investigated by calculating the Ef of the substitutional Eu (EuZn) and interstitial Eu (EuI) in the stochiometric ZnO as presented in Table 1.

Table 1

The Ef	Eu's Spin Number	Magnetic Ground State
ZnO:EuZn	-2.391	6.800 Paramagnetic
ZnO:EuI	1.429	6.859 Paramagnetic
ZnO:EuZn + VO	1.772	6.907 Paramagnetic
ZnO:EuZn:ZI	2.776	6.879 Ferromagnetic

The Ef, Eu's spin number, and the magnetic ground state of the ZnO:EuZn, ZnO:EuI, ZnO:EuZn + V and ZnO:EuZn + ZnI are presented. Configuration Ef (eV) Eu's spin ([ℏ]/2) Magnetic ground state

It was found that the Ef of EuZn is -2.391 eV while the Ef of EuI is 1.429 eV. Such a large difference in Ef indicates that Eu ions favorably substitute Zn ions rather than taking the interstitial sites of the ZnO lattice. The local geometry of the EuZn and EuI is presented in (a) and (b). Figure 1a shows that the length of Eu-O bond along c direction (ab plane) has increased to 2.280 Å (2.260 Å) in the ZnO:EuZn system. The increase of the bond lengths is approximately equivalent to an expansion of 14% along the c direction and 13% within the ab plane with respect to the Zn-O bond length in an undoped ZnO. On the other hand, in the ZnO:EuI system, in which EuI binds to three Zn and three O ions, the length of the Eu-O and Eu-Zn bonds were found to be 2.323 and 2.857 Å comprising an expansion of 16% and 24%, respectively compared to the unrelaxed structure. In the ZnO:EuZn system, although the length of the Eu bonds is also substantially expanded, the expansion is much smaller than that in the ZnO:EuI system. As a result, the ZnO:EuZn system reaches the structural stability with less lattice distortion.

Results & Discussion: The Ef of EuZn in the nonstochiometric ZnO was studied by considering two distinct situations that lead to Zn excess: first by including a VO in the ZnO:EuZn + VO system and then by including a ZnI in the ZnO:EuZn + ZnI system. The Ef of the EuZn + VO and EuZn + ZnI complexes in the ZnO lattice was found to be 1.772 and 2.776 eV, respectively. The local geometry of the Eu ion in the ZnO:EuZn + VO and ZnO:EuI + VO are presented in Figure 1c, d respectively. In the ZnO:EuZn:VO system, the length of the Eu-O bond is 2.280 along the c direction and 2.260 within the ab plane, which is identical to the bond length in the ZnO:EuZn system without VO.However, in the ZnO:EuZn+ZnI system, the length of the Eu-O bond expanded to 3.517 Å along the c direction and 3.344 Å within the ab plane. Such an expansion corresponds to a 75% and 67% increase in the length of the Eu-O bonds along the c direction and within the ab plane, respectively compared to the unrelaxed structure. As a result, the EuZn + ZnI complex has the highest Ef and lattice distortion. To investigate the electronic properties of the ZnO:Eu systems, the total and Eu's 4f partial density of states (DOS) of all configurations were calculated and presented in Figure 2. A general feature of the Eu's 4f states in all configurations is that Eu's 4f states are localized in a narrow impurity band of the width of approximately 1 eV, which is located just below the Fermi level. Such localization of the 4f states indicates that 4f electrons are not affected by the local crystal environment. This point is further reinforced by the Eu's magnetization as presented in Table 1. The spin number (S) of the Eu ions in all configurations is approximately 6.9, very close the spin number of free Eu atoms which indicates the infinitesimal hybridization of Eu's f orbitals with other orbitals in the host crystals. According to Figure 2a, b, in stochiometric systems, ZnO:EuZn and ZnO:EuI, there are minor electronic states available at the Fermi level resulting in limited mobile carriers in those systems. However, this amount of carriers is not sufficient to establish carrier-mediated magnetism in the stochiometric ZnO:Eu systems, and these systems remain paramagnetic [24]. By introducing VO, in the ZnO:EuZn + VO system, the VO's impurity states appear below Eu's 4f states as shown in Figure 2c. Thus, VO does not enhance the carrier concentration in the ZnO:EuZn + VO system either. As shown in Figure 2d in the ZnO: EuZn + ZnI system, ZnI's 4s states appear in a small peak at the Fermi level, partially hybridizing with Eu's 4f states and introducing further carriers at the Fermi level. To investigate the possibility of ferromagnetic coupling in the defective systems, two substitutional Eu ions were located in the supercells. Then the Ef of each system was calculated once for ferromagnetic magnetic alignment (EFM) and once again for antiferromagnetic magnetic alignment (EAFM) of the Eu ions. Finally, ΔE is

defined to be EAFM - EFM which is an indicator of ferromagnetic phase stabilization. For Eu ions separated by approximately 3.4 Å (nearest possible distance), ΔE was found to be 21 meV for the ZnO:Eu + ZnI system and 3 meV for the ZnO:Eu + VO system. However, for both systems, the ΔE vanishes when the separation between the Eu ions increases to approximately 6 Å.This trend in ΔE indicates that ZnI induces short range ferromagnetic coupling in the ZnO:Eu system.

Conclusion: The structural and electronic properties of the ZnO:Eu systems were investigated by ab initio technique It was found that Eu ions substitute Zn sites in the ZnO host lattice favorably. With excess in the ZnO:Eu system, the carrier-mediated ferromagnetism can be induced by ZnI. Clearly whenever ferromagnetism is induced the applications are increased significantly. Moreover, ZnO doped Eu and their systems have many interesting potential applications such as transparent electrode, piezoelectric device, and gas sensor and it can be used as windows layer in heterojunction solar cells also.

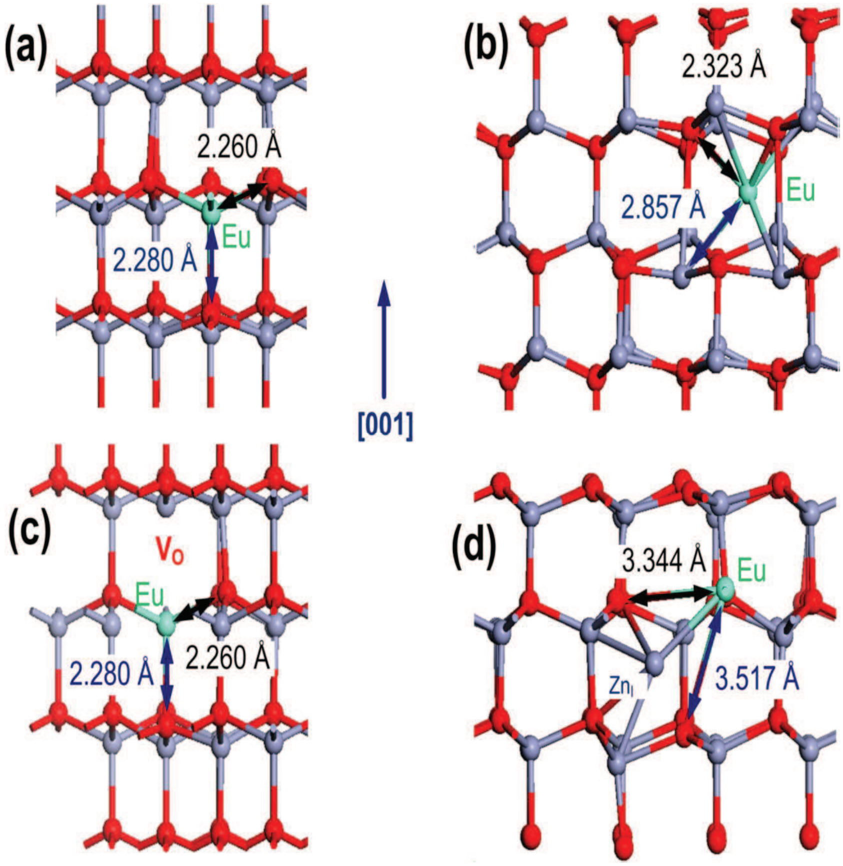

Figure 1. The relaxed crystallographic structure of the ZnO:Eu systems. Representing (a) ZnO:EuZn, (b) ZnO:EuI, (c) ZnO:EuZn + VO, (d) ZnO:EuZn + ZnI systems. Red, blue, and gray balls represent the O, Zn, and Eu ions, respectively. For each system, the calculated length of the Eu bonds is presented along both the c direction (or [001]) and within the ab (basal) plane

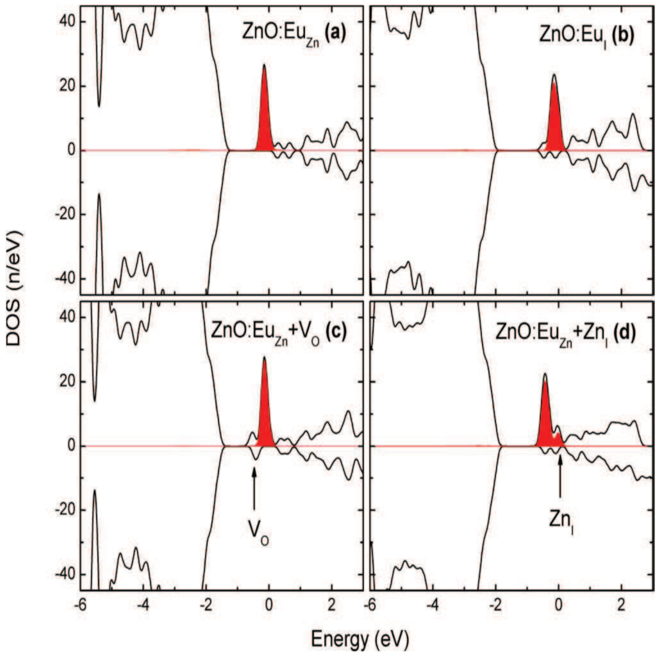

Figure 2. Total and partial DOS of the ZnO:Eu systems. Representing (a) ZnO:EuZn, (b) ZnO:EuI, (c) ZnO:EuZn + VO, (d) ZnO:EuZn + ZnI systems. The solid black lines and the red-shaded areas represent the total and Eu's partial 4f states, respectively. Also, energy is represented with respect to the Fermi level.

Abbreviations:
DFT: density functional theory; DMS: diluted magnetic semiconductors; DNP:double numerical polarized; DOS: density of states; GGA: generalized gradient approximation; PDOS: partial density of states.

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