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Interactions Between Zinc Oxide and Alkali Metals, Alkaline Earth Metals and Halogens: A Theoretical Study

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Zinc oxide is a multifunctional material due to its incredible physical and chemical properties. The aim of this work is to analyze the interactions between zinc oxide and different elements and depict how the structure and energy are modified by their presence. We focused on elements of groups IA, IIA and VIIA of the periodic table and for simplicity, only atoms from periods 1-4.

Keywords: ZnO, Theoretical, CCD.

INTRODUCTION

The extraordinary properties of ZnO such as being thermoluminescent under irradiation with different sources, inert to environmental conditions, non-toxic, insoluble in water [1] and having low thermal expansion, high heat capacity, heat conductivity, melting temperature, piezoelectric tensor and a relatively large band gap make it a versatile material with a wide variety of breakthrough applications in electronics, medicine, optoelectronics, laser technology, among others [2]. Precisely, it has been reported that the 3.4 eV band gap of ZnO can be modified through the use of dopants such as cadmium and magnesium [3]. Despite the intentional modification of their geometries, hydrogen impurities, oxygen vacancies and interstitial Zn ions play an important role in the structure and properties of the resulting ZnO crystal [4].

Recently, it has been reported that ZnO is a promising dosimetric material due to its thermoluminescent behaviour upon exposure to irradiation and its striking radiation hardness [5]. However, its application in radiation dosimetry has only been slightly studied. Many thermoluminescent phosphor materials, synthetic as well as natural, have been characterized in order to evaluate its feasibility as thermoluminescent (TL) dosimeters (TLD), applicable in several dosimetry areas, from X-ray medical diagnose and radiotherapy to radiological protection [6].

Although ZnO has a wide variety of applications, its interactions with groups IA, IIA and VIIA of the periodic table have not been fully explored. Only a few works have theoretically studied interactions between ZnO and other elements [7,8]. Our main concern is to analyze the properties of ZnO alone and of the systems formed by interacting with the elements aforementioned. These results will provide an interesting insight for future experiments. Eventually, it can lead to a better understanding of the behaviour of certain metals in the presence of ZnO and hopefully create an impact on its applications.

COMPUTATIONAL METHODS

The theoretical calculations were carried out with the GAUSSIAN09 software [9]. The main interactions in the systems studied herein are van der Waals forces. Although density functional theory (DFT) methods have been extensively used in the past years, but they fail in the calculation of dispersion forces. Therefore, we have applied an *ab initio* technique that takes into account long-range interactions more adequately than DFT methods. We employed the double excitation coupled cluster (CCD) methodology [10] in conjunction with the quadruple zeta valence plus polarization basis set (QZVP) [11].

To verify that the energies yielded were accurate enough within the theoretical framework, a tight convergence criteria was employed. Hessian matrix elements were also evaluated to check if the structures are energy minima systems along the potential energy surface. Only structures with positive vibrational frequencies were considered as energy minima structures since the presence of a negative frequency indicates a transition state. Experimentally, it is possible to prove this due to the fact that the spectra shows exclusively the energy minima structures.

The dissociation energies (ΔE) of the systems were calculated to set their stability as follows:

$$\Delta_E = E_{Z(ZnO)} - (E_Z + E_{ZnO})$$

where Z stands for an element (either a metal or a halogen) and Z(ZnO) represents the system formed by the interaction between ZnO and the element.

The fit for enthalpy reported on this manuscript was performed according to the equations implemented by the National Institute of Standards and Technology NIST [12]. These equations have been very good at predicting physical properties of various molecules, as it has been tested in the past [13-15].

RESULTS AND DISCUSSION

Zinc oxide has a bond distance of 1.74 Å and a HOMO/LUMO band gap of 8.535 eV. These values are modified in the presence of other elements. Our main interest is to study the interactions between ZnO and elements of groups IA, IIA and VIIA. To establish a comparison between these groups we have selected atoms of the first 4 periods. Table-1 lists the physical properties of the structures formed by ZnO and an element, where ΔE (0K) corresponds to the dissociation energy with a zero-point correction at the CCD/QZVP level and GAP stands for the HOMO/LUMO band gap in eV. Table-2 displays the enthalpy of the systems at 100 K, 298 K and 1000 K by obtaining a fit to the Shomate equation [12]. The systems formed by the interaction between the elements with Zn in ZnO are represented by Z-ZnO, while the ones interacting with O in

TABLE-1
DISSOCIATION ENERGIES WITH ZERO-POINT CORRECTIONS ARE DENOTED BY ΔE (0 K, kcal/mol) AND HOMO/LUMO BAND GAPS (eV) ARE LISTED UNDER GAP CALCULATED AT THE CCD/QZVP LEVEL FOR THE SYSTEMS Z-ZnO AND ZnO-Z

System	ΔE (0 K)	Gap	System	ΔE (0 K)	Gap
H-ZnO	-75.067	13.478	Cl-ZnO	-96.971	13.160
Li-ZnO	-51.003	7.076	Br-ZnO	-94.450	12.341
Na-ZnO	-29.289	6.575	ZnO-Li	-95.272	7.128
K-ZnO	-31.469	5.582	ZnO-Na	-72.300	6.279
Be-ZnO	-7.279	6.885	ZnO-K	-68.074	5.817
Mg-ZnO	-10.550	6.694	ZnO-Mg	-59.693	3.673
Ca-ZnO	-18.300	5.517	ZnO-Ca	-79.313	3.021
F-ZnO	-112.784	14.810	ZnO-Br	-45.180	9.799

TABLE-2
STANDARD ENTHALPY (ΔH, KJ/mol) AT 100 K, 298.15 K AND 1000 K CALCULATED AT CCD/QZVP LEVEL. THESE WERE FITTED TO SHOMATE EQUATIONS WHICH ARE IMPLEMENTED BY JANAF TABLES OF NIST DATABASES. THE EQUATIONS CONVERGED TO AN R^2 VALUE OF 0.99 ON AVERAGE

System	Fitted equation ΔH (KJ/mol) $t = 1/T$	100 K	298.15 K	1000 K
H-ZnO	$14249.276 - 4891767.697\ t^2/2 -168088231.401\ t^3/3 + 109465108154.704\ t^4/4 + 0.006/t - 84015.178\ t/1.5 - 36.083$	-2.900	-7.740	-20.950
Li-ZnO	$-25778.919 - 46725715.651\ t^2/2 + 6447983877.904\ t^3/3 - 417926617018.808\ t^4/4 - 0.013/t + 2169926.570\ t/1.5 + 5.084$	-2.500	-5.600	-14.260
Na-ZnO	$27031.731 + 42701321.199\ t^2/2 - 5314247819.275\ t^3/3 + 321613756243.757\ t^4/4 + 0.006/t - 213362.852\ t/1.5 -10.566$	-0.810	-0.080	3.300
K-ZnO	$-29969.503 - 51349524.317\ t^2/2 + 6920618026.989\ t^3/3 - 442683804375.408\ t^4/4 - 0.014/t + 2433233.208\ t/1.5 + 9.073$	-2.010	-4.350	-12.510
Be-ZnO	$10950.734 + 18132414.692\ t^2/2 - 2334863991.173\ t^3/3 + 144032206967.084\ t^4/4 + 0.005/t - 876106.784\ t/1.5 - 5.453$	-0.950	-0.600	2.240
Mg-ZnO	$7913.778 + 13918939.824\ t^2/2 - 1837822820.780\ t^3/3 + 114763366244.262\ t^4/4 + 0.004/t - 657511.123\ t/1.5 - 3.595$	-0.750	-0.170	2.740
Ca-ZnO	$-31989.534 - 56696853.696\ t^2/2 + 7693452339.198\ t^3/3 -492893074243.688\ t^4/4 - 0.014/t + 2658602.298\ t/1.5 + 8.348$	-1.960	-4.570	-2.610
F-ZnO	$-32588.128 -58324467.489\ t^2/2 + 7839634019.009\ t^3/3 - 499026352586.676\ t^4/4 - 0.014/t + 2740742.226\ t/1.5 + 5.451$	-2.630	-6.430	-16.150
Cl-ZnO	$8639.990 + 15352393.694\ t^2/2 - 2072477085.264\ t^3/3 + 131002137898.968\ t^4/4 + 0.004/t - 715524.500\ t/1.5 -5.668$	-1.430	-1.630	0.930
Br-ZnO	$9217.209 + 16052745\ t^2/2 -2097394813.631\ t^3/3 + 129557804962.545\ t^4/4 + 0.004/t - 760593.491\ t/1.5 - 5.138$	-1.310	-1.170	1.680
ZnO-Li	$5666.450 + 6888352.624\ t^2/2 - 890016015.350\ t^3/3 + 57297880177.850\ t^4/4 + 0.004/t - 360811.439\ t/1.5 -7.141$	-1.280	-1.910	-0.630
ZnO-Na	$-3036.487 - 2700270.130\ t^2/2 + 149481888.571\ t^3/3 -2302388437.507\ t^4/4 + 0.003/t + 184735.466\ t/1.5 - 0.801$	-1.080	-1.080	1.290
ZnO-K	$-216.428 + 2646913.097\ t^2/2 - 574117456.899\ t^3/3 + 43838661613.081\ t^4/4 + 0.003/t - 63137.546\ t/1.5 -0.903$	-1.020	-0.720	1.880
ZnO-Mg	$-37946.418 - 67840201.320\ t^2/2 + 9101187088.470\ t^3/3 -577331527639.916\ t^4/4 - 0.014/t + 3187003.721\ t/1.5 + 7.514$	-2.520	-6.050	-15.890
ZnO-Ca	$12296.978 + 19024980.287\ t^2/2 -2378910555.565\ t^3/3 + 144279253818.101\ t^4/4 + 0.005/t - 943027.099\ t/1.5 - 6.510 + t^2/2+ t^3/3+ t^4/4+/t+ t/1.5+$	-0.690	-0.520	2.030
ZnO-Br	$-6.240 -2482920t2/2 + 483916500t3/3 -27744328000t4/4$	-1.270	-2.530	-3.610

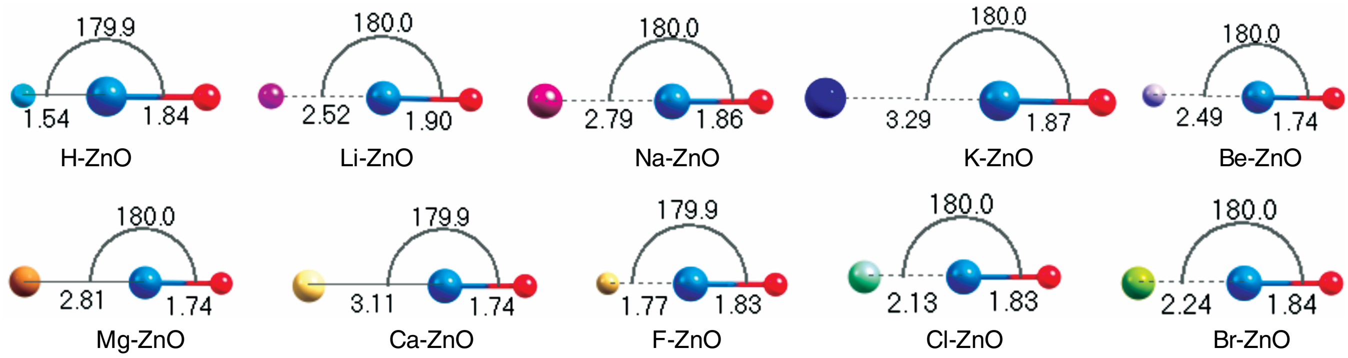

Fig. 1. Selected geometrical parameters of the Z-ZnO systems, where distances are expressed (Å) and angles (°)

ZnO are represented by ZnO-Z. Fig. 1 (Z-ZnO) and 2 (ZnO-Z) show geometrical parameters of the systems.

The first structure in Fig. 1, H-ZnO, forms an interaction with Zn with at 1.54 Å and an angle of 179.9° which stabilizes the system with a dissociation energy of -75.067 kcal/mol and a HOMO/LUMO band gap of 13.478 eV. The system Li-ZnO, interacts at a distance of 2.52 Å. Thus, it is less stable than H-ZnO, with a dissociation energy of -51.003 kcal/mol. Its gap is of 7.076 eV, which indicates that it has a more metallic nature and a smaller probability of being thermoluminescent. The next metal in group IA is Na, which interacts with ZnO at a longer distance than Li-ZnO of 2.79 Å. Since Na is larger than Li, the repulsion between Zn and Na is larger and therefore the stability is reduced, with an energy of -29.289 kcal/mol. Its band gap is slightly smaller than that of Li, making it more metallic. As the size of the metal increases, the distance between the metal and Zn increases too. In the case of K-ZnO, the metals interact at 3.29 Å. Its dissociation energy of -31.469 kcal/mol is more negative than that of Na-ZnO probably due to the higher polarizability of K, which contributes to a more stable system. Its HOMO/LUMO band gap is smaller, with a value of 5.582 eV, yielding a metallic interaction.

The metals of group IIA have no unpaired electrons. This causes a smaller metallic interaction than in atoms of group IA, which have one unpaired electron. It can be observed that the interaction occurs mainly with Zn, while the distance ZnO remains unchanged. However, in all other cases, the distance ZnO is modified. The first atom, Be interacts with ZnO at a distance of 2.49 Å and a dissociation energy of -7.279 kcal/mol. The HOMO/LUMO band gap is of 6.885 kcal/mol. This value is similar to the ones of group IA elements probably in both cases the interactions are of a metallic nature and could be less prone to thermoluminescence. Magnesium interacts with ZnO at a larger distance than Be, 2.81 Å most likely because of its larger size. Its stability is greater than in Be-ZnO, with a value of -10.550 kcal/mol probably due to the fact that the polarizability of Mg is higher than that of Be. Its band gap is of 6.694 eV, slightly smaller than that of Be-ZnO. The last element in group IIA, Ca interacts with ZnO at 3.11 Å. Its higher stability could be due to the polarizability of Ca, yielding a dissociation energy of -18.300 kcal/mol. The band gap is reduced to 5.517 eV, reflecting that the interaction is less metallic.

The elements in group VIIA form the most stable systems with ZnO. It is interesting to note that H behaved as an element in this group since its energy and HOMO/LUMO band gap was more similar to those of group VIIA than those of group IA. The elements in this group have higher band gaps, making it certain that they are more apt for thermoluminescence than the atoms in groups IA and IIA. Furthermore, the atoms in group VIIA formed the most stable systems due to their ability to attract electrons from Zn to form a bond. Fluorine is the most electronegative element in the periodic table. Therefore, its interaction with Zn should be the strongest. Its dissociation energy of -112.784 kcal/mol confirms its high stability at 1.77 Å. Its band gap is of 14.810, which indicates a better disposition for thermoluminescence. Chlorine forms a bond at 2.13 Å with a HOMO/LUMO band gap of 13.160 eV and has a dissociation energy of -96.971 kcal/mol. Its lower stability than that of F-ZnO could be caused by the steric repulsion due to the larger size of Cl. Bromine forms a bond at 2.24 Å, with a lower band gap of 12.341 eV. This can be owed to the lower electronegativity of Br compared to Cl. The dissociation energy of this system is of -94.450 kcal/mol, which is slightly less stable than the system of Cl. This can be owed to the larger size of Br and thus increased repulsion.

Fig. 2 displays the systems ZnO-Z. It is interesting to note that several atoms only formed transition states when interacting directly with oxygen in ZnO and not energy minima structures. The first element that did not form a stable system was hydrogen. Oxygen gains 2 electrons from zinc and thus acquires a closed shell. The interaction between hydrogen and oxygen is *via* van der Waals forces, which are not strong enough to stabilize the system. In the case of ZnO-Li, a bond of 1.64 Å is formed between oxygen and lithium. The extraordinary electron donor properties of lithium promote a highly stable system, with a dissociation energy of -95.272 kcal/mol. Its band gap of 7.128 eV is mildly different than that of Li-ZnO. ZnO-Na interacts at a distance of 2.02 Å and an energy of -72.300 kcal/mol. In comparison to ZnO-Li, it has a higher energy most likely because the larger size of the metal causes more repulsion with oxygen. However, the band gap is reduced to 6.279 eV. The last metal of group IA we considered was potassium, which is attracted to oxygen at a distance of 2.44 Å. Following the pattern of this group, as the size of the metal increases, the interaction with oxygen is less strong, yielding a dissociation energy of ZnO-K of -68.074 kcal/mol. The HOMO/LUMO band gap also follows a trend by being reduced to 5.817 eV.

The first metal in group IIA is Be, which does not donate electrons as strongly as lithium and forms a transition state

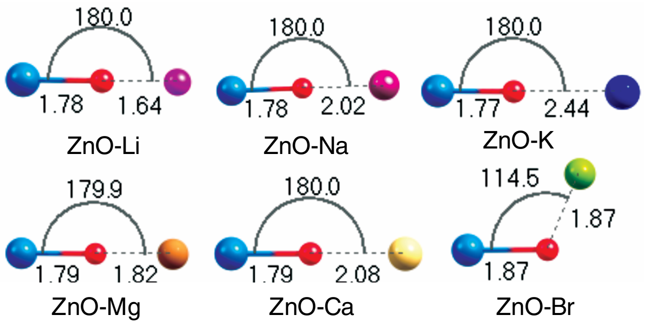

Fig. 2. Selected geometrical parameters of the ZnO-Z systems, where distances are expressed (Å) and angles (°)

but not a global energy minima. Magnesium interacts with oxygen in ZnO-Mg at a distance of 1.82 Å. Its larger size induces the energy to rise to a value of -59.693 kcal/mol, while its band gap of 3.673 eV, indicates a low disposition towards thermoluminesence. Calcium, as a good electron donor forms a more stable system than Mg-ZnO, at a distance of 2.08 Å and a dissociation energy of -79.313 kcal/mol. Anyhow, it follows the tendency and its band gap decreases to 3.021 eV.

The high electronegativity of fluorine affects negatively the formation of ZnO-F since -1 is its single oxidation state. Its only possibility is to attract the closely packed electrons from oxygen, which has gained a closed shell by forming the ionic compound ZnO. Thus, the system ZnO-F is not a stable system. Chlorine has also a high electronegativity, which most likely inhibits the stabilization of the system ZnO-Cl. Bromine, aside from being less electronegative than chlorine and fluorine, it has positive oxidation states aside from -1. Hence, its interaction with oxygen could be due to a charge transfer from the bromine to oxygen. This could affect the formation of a stable ZnO-Cl system. In the case of ZnO-Br, it forms a non-linear stable system at 1.87 Å, an angle of 114.5° and a dissociation energy of -45.180 kcal/mol. Its high HOMO/LUMO band gap value of 9.799 could signify a high thermoluminescent ability.

In addition to dissociation energy, we gave calculated enthalpy to corroborate the stability of the systems. As we can see in Table-2, at high temperatures, some of them have positive values. This behaviour is expected, since at high temperature, a system could gain enough kinetic energy to change its configuration. However, our main interest relies at lower temperatures like room temperature. The results show that the value of the enthalpy is negative at 100 K and 298.15 K for all the systems, which confirms the stability of the systems. This is in agreement with the negative values of the dissociation energies of all the systems.

Conclusions

The results showed that all the systems have negative values for their dissociation energies and enthalpies, which leads us to the conclusion that they are stable. The first set of systems, Z-ZnO shown in Fig. 1 had metallic interactions when Z was a alkali or alkali-earth metal, except for hydrogen and non-metallic when Z was a halogen. All of the systems were stable, with varying energies and HOMO/LUMO band gaps. Group IA and IIA metals had similar band gaps, which signifies they have a similar thermoluminescent ability. Group IA interacted stronger with Zn in ZnO probably because of their one unpaired electron has a higher contribution to a metallic interaction. Hydrogen, on the other hand, behaves more similarly to group VIIA nonmetallic atoms. Halogens formed the most stable systems due to their electronegativity and the highest band gaps, which should imply a better predisposition towards thermoluminescence.

The second set of ZnO-Z structures displayed in Fig. 2 show ionic interactions for metals in group IA and IIA and nonmetallic interactions for group VIIA atoms. It is interesting to note that not all elements formed stable global energy minima. Electronegativity could be a strong cause for atoms such as hydrogen, beryllium, fluorine and chlorine not to stabilize the system. The most stable systems were ZnO-Li and ZnO-Ca presumably because of their strong ability of donating electrons. Group IA band gaps remained almost unchanged comparing Z-ZnO and ZnO-Z values. However, group IIA ZnO-Z structures yield smaller band gaps than those of Z-ZnO showing that the last ones could be more apt for thermoluminescence. Despite its lower stability compared to the rest of the systems of ZnO-Z, ZnO-Br has the largest gap and hence has a higher affinity towards thermoluminescence. However, Br-ZnO has a higher band gap and is more stable than ZnO-Br, showing that bromine would prefer interacting with zinc than oxygen yielding a more thermoluminescent system.

The importance of this study is not only to discuss which systems can be formed, but from those that are actually formed select which have a better disposition towards thermoluminescence. As we have discussed, the interaction of ZnO with other elements modifies the HOMO/LUMO band gaps and energies of the structures formed, influencing its possible applications. It is our aim to compare our results to experiments and use them in the design of new experiments and thermoluminescent materials.

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