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HYDROGEN STORAGE IN SOLIDS: A CASE STUDY

Physics

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ABSTRACT

The density functional theory (DFT) has been used to study ground state structural properties of BeH_2 (space group- Ibam) and MgH_2 (space group- $P4_2/mnm$). The calculations have been performed using full-potential linearized augmented plane waves (FP-LAPW) method. The obtained unit cell lattice constants of BeH_2 and MgH_2 are in excellent agreement with the earlier reported data. Further, we have extended our calculations to find out the unit cell lattice parameters for extra hydrogen added structures (BeH_2+2H, BeH_2+4H, MgH_2+4H and MgH_2+8H). On the basis of the obtained results it has been found that the stability of structure increases with the increase in number of added hydrogen atoms. Thus, we can say that BeH_2 and MgH_2 can be used for the purpose of hydrogen storage.

INTRODUCTION

Energy supply for the future is one of the most important dilemmas to be faced by the mankind. Answer to this problem requires research and solution of problems related to novel energy sources, energy storage and transportation. It is difficult to imagine that any significant breakthrough can be done without inventions of new materials with strictly designed properties. In particular new solutions are required for energy storage for mobile applications, like electronic devices (portable electronics) or road transportation (automobiles). Also, new solutions are needed for energy load leveling from power stations that use renewable energy sources like wind or solar [1]. The search for new potential compounds with desired properties for hydrogen storage has been a continuous challenge among researchers during past few decades [2, 3].

Hydrogen is the ideal candidate as an energy carrier for both mobile and stationary applications while averting adverse effects on the environment, and reducing dependence on imported oil for countries without natural resources. Hydrogen storage is clearly one of the key challenges in developing hydrogen economy. Hydrogen can be stored as (i) pressurized gas, (ii) cryogenic liquid, (iii) solid fuel as chemical or physical combination with materials, such as metal hydrides, complex hydrides and carbon materials, or produced on-board for the vehicle by reforming methanol [4]. Each of these options possesses attractive attributes for hydrogen storage [5].

At present, majority of energy for transportation comes from crude oil (gasoline or diesel fuels) and several means of energy storage are available, they include: batteries, capacitors or hydrogen fuel cells for electric energy. In this communication we mainly focus on metal hydrides as a solid state hydrogen storage compounds.

Metal hydrides are reversibly formed for selected metals or alloys exposed to high pressures of hydrogen. For light metals, such as alkaline earth metal, we obtain relatively good storage density; however catalysts are requires for the full reversibility of storage in Mg, Li or similar metals [6].

Hydrogen forms metal hydrides with some metals and alloys, leading to solid state hydrogen storage under moderate temperature and pressure, are very safe as compare to the gas and liquid storage methods. Metal hydrides have higher hydrogen-storage density (6.5 H atoms/cm3 for MgH2) than hydrogen gas (0.99 H atoms/cm3) or liquid hydrogen (4.2 H atoms/cm3) [7]. Hence, metal hydride storage is a safe, volume efficient storage method for on-board vehicle applications.

An ideal hydrogen storage material is supposed to have high gravimetric hydrogen density and alkaline earth metal hydrides are novel choice for this criteria. Moreover, the formation energy of such a material has to be such that it is stable at room temperature, yet it has to decompose at low temperature to release its hydrogen. Besides alkaline metal hydrides; alkali hydrides, amides, borates and alanates are also known to be hydrogen storage compounds with several promising applications [8-11]. In principle a large variety of hydrides (e.g. alanates and boranates) can be synthesized by changing the metal cations, which can be used to tune the formation energy [12].

Such information can be provided on theoretical basis, and it requires extensive search for the ground state structures and their properties by quantum methods. As such searching of the ground state structure of compounds is a complex problem.

COMPUTATIONAL DETAILS

The calculation described in this communication was based on density functional theory (DFT). For the calculation we employed the full potential linearized augmented plane wave method (FP-LAPW) as implemented in the Wien2k code [13]. We expand the basis function up to $R_{MT}*k_{max}=7$, where RMT is the smallest radius of the muffin-tin (MT) spheres and k_{max} is the maximum value of the reciprocal lattice vectors. The maximum l value for the wave function expansion inside the atomic spheres was confined to $l_{max}=10$. The k-points used in the calculations were based on 10*10*10 Monkhorst-Pack scheme. The iteration process was repeated until the calculated total energy and charge of the crystal converges to less than 0.0001Ry and 0.001e- respectively.

RESULTS AND DISCUSSION

In MgH2 and BeH2 the atomic number of Mg, Be and H are 12, 2 and 1, respectively. The electronic configuration of Mg and Be are [Ne] 3s2, 1s2 , respectively and that of H is 1s1. The ground state structure of MgH2 is rutile type (space group- P42/mnm) and that of BeH2 is body centered orthorhombic structure (space group- Ibam). In DFT the essential parameters for optimization are unit cell parameters, atomic positions of respective elements and Muffin tin radius (RMT) of the constituent elements. TABLE 1 summarizes used values of RMTs and atomic positions of constituent atoms.

TABLE – 1
Muffin tin radius (RMT) in a.u. and atomic positions of constituent's atoms

Material	Atom	RMT	Atomic position
MgH_2+0H	Mg	1.8	0.0, 0.0, 0.0
	H	1.2	0.3043,0.3043, 0.0
	H*	--	-- -- --
MgH_2+4H	Mg	1.5	0.0, 0.0, 0.0
	H	1.3	0.3043,0.3043, 0.0
	H*	1.2	0.0, 0.0, 0.65

MgH_2+4H	Mg	1.5	0.0, 0.0, 0.0
	H	1.3	0.3043,0.3043, 0.0
	H*	1.2	0.0, 0.0, 0.65
MgH_2+8H	Mg	1.5	0.0, 0.0, 0.0
	H	1.3	0.3043,0.3043, 0.0
	H*	1.2	0.65, 0.65, 0.65
BeH_2+0H	Be	1.5	0, 0, 0.25
	Be	1.5	0.1699, 0.1253, 0
	H	1.0	0.0895,0.1949, 0.1515
	H	1.0	0.3055, 0.2823, 0
	H*	--	-- -- --
BeH_2+2H	Be	1.5	0, 0, 0.25
	Be	1.5	0.1699, 0.1253, 0;
	H	1.0	0.0895,0.1949, 0.1515
	H	1.0	0.3055, 0.2823, 0
	H*	1.4	0, 0, 0
BeH_2+4H	Be	1.5	0, 0, 0.25
	Be	1.5	0.1699, 0.1253, 0
	H	1.0	0.0895,0.1949,0.1515
	H	1.0	0.3055, 0.2823, 0
	H*	1.2	0, 0, 0.4

H* denotes the added hydrogen atoms

By using the available data in literature we optimized the structure of MgH_2 and BeH_2. Optimized values for unit cell volume and corresponding energy are fitted to Murnaghan's equation of state [14] to make the volume versus energy curves (not shown here). From the optimized unit cell volume we have calculated the lattice parameters of MgH_2 and BeH_2. Theoretically optimized structural parameters for MgH_2 and BeH_2 along with corresponding experimentally observed values are listed in TABLE 2. The obtained unit cell dimensions for MgH_2 and BeH_2 are in very good agreement with data reported in the literature [10-13]. The theoretical calculations also identify the tetragonal rutile-type and body centered orthorhombic phase as the ground state structure of MgH_2 and BeH_2, respectively.

We have extended similar studies of simulation for extra hydrogen added structures; BeH_2+2H, BeH_2+4H, MgH_2+4H and MgH_2+8H, in order to optimize the structural parameters. The optimized unit cell parameters for BeH_2+2H, BeH_2+4H, MgH_2+4H and MgH_2+8H are listed in TABLE 2. It is evident from TABLE 2 that the optimized equilibrium volume of MgH_2+8H > MgH_2+4H > MgH_2 while the equilibrium total energy of MgH_2+8H < MgH_2+4H < MgH_2. Similarly, in case of BeH_2 the optimized equilibrium volume of BeH_2+4H > BeH_2+2H > BeH_2 while the equilibrium total energy of BeH_2+4H < BeH_2+2H < BeH_2. This reveals the fact that with the stability of structures increase as the number of extra added hydrogen atoms increases.

TABLE – 2
Calculated structural parameters and optimized energy of studied structures

Material	Lattice parameters			Energy	Ref.
	a	b	c		
MgH_2+0H	4.505	4.505	3.012	-806.08	[15, 16]
MgH_2+4H	6.794	6.794	4.543	-809.72	
MgH_2+8H	6.943	6.943	4.642	-814.36	
BeH_2+0H	9.246	4.235	7.846	-191.28	{17, 18]
BeH_2+2H	9.475	4.341	8.091	-193.20	
BeH_2+4H	10.078	4.616	8.553	-194.90	

CONCLUSIONS

The obtained values of structural parameters for BeH2 and MgH2 are in excellent agreement with the available experimental and theoretical data. The results related to extra hydrogen compounds (BeH2+2H, BeH2+4H, MgH2+4H and MgH2+8H) are reported first time. The stability of structures increases as number of added hydrogen increases and the energy will also further minimize if the number of added hydrogen is large. Thus, we conclude that alkaline hydrides are very suitable for hydrogen storage.

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