Structural stability, electronic, and mechanical properties of new stable phases for the ternary alloy $Mg_xCd_{1-x}O$

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Abstract

With the development of technology, finding new crystallographic phases with remarkable properties and that are easy to be elaborated experimentally is highly recommended. The II-VI semiconductors are very interesting materials for various applications due to the possibility to preselect and control their physical properties; which can be realized by varying the atomic concentration to form alloys. Herein, density functional theory (DFT) calculation has been performed for the alloy $Mg_xCd_{1-x}O$ to investigate the thermodynamic, dynamical, and local stability of $MgCdO_2$ for 50% of concentration and $MgCd_3O_4$ for 25%. $MgCdO_2$ is stable in a tetragonal phase whereas, the $MgCd_3O_4$ is not stable in the same cubic phase predicted for 75% (Pm-3m) in the previous work, instead, it is stable in another cubic phase (P-43m). the elastic constants and mechanical properties predict that adding Mg atoms to the alloy enhance the resistance of the material.

Keywords

$Mg_xCd_{1-x}O$, II-VI semiconductors, structural stability, mechanical properties.

Introduction:

Wide band gap II-VI semiconductors alloys are very interesting candidates for high performance optoelectronic devices in the blue and ultraviolet electromagnetic regions, such as light emitting diodes (LEDs) and laser diodes [1]–[4]. Despite the important properties of this type of semiconductors, the modulation of some of it is necessary. Among the options to control and modulate a property of a material is to form alloys, which can be stable in different possible phases.

In recent years, after all the achievements realized by researchers in the condensed matter field, using density functional theory (DFT); the experimenters are far from keeping pace with this development due to a lot of difficulties to calibrate the experimental parameters. Finding new stable phases may not only improve the properties of a system but also might facilitate its experimental study.

This work is an extension of our latest paper on the ternary alloy $Mg_xCd_{1-x}O$ studied in a new possible phase, wherein only the stability of Mg_3CdO_4 that refers to an atomic fraction of 75% was investigated along with its mechanical and optoelectronic properties [5]. In this paper, MgCdO2 for 50 % of concentration and $MgCd_3O_4$ for 25 % were studied for other phases in which the structural stability, and mechanical properties were discussed.

Computational details:

Based on Density functional theory (DFT) [6], the calculation was carried out by solving iteratively the Kohn-Sham equation as implemented in Wien2k and Quantum ESPRESSO simulation package codes [7], [8]. The exchange correlation potentials are treated using the generalized gradient approximation (GGA) in the form of Perdew, Burke and Ernzerhof (PBE) functional [9]. The electronic properties were calculated using Wien2k and improved with modified Becke-Johnson exchange potential by Tran and Blaha (TB-mbj-GGA) correction [10]. For x= 0.25, the material crystallizes in P-43m cubic space group; on the other hand, for x= 0.50 it crystallizes

in a tetragonal phase P4/mmm. For the Full-Potential Linearized Augmented Planewave Method (FPLAPW) [11], The muffin-tin radii for Mg, Cd and O are 2.03, 2.18 and 1.87 Bohr, respectively. The cut-off energy and the plane wave cut-off $RMT \times k_{max}$ were set by default. Further, the pseudo-potential plane wave method (PW-PP) using Ultrasoft pseudo-potential (USPP) [12] was used to describe the ion-electron interaction, with cutoff energies of 60 Ry and 600 Ry for the wave functions and the charge density respectively. The Brillouin zone was sampled with k-points meshes 11×11×11 based on the method of Monkhorst-pack (MP) [13] for the cubic structure and of 12×12×9 for the tetragonal structure. The self-consistent total energy calculation was set up to converge toward 10^{-4} Ry. The phonon properties are calculated using the density functional perturbation theory (DFTP) [14]. A 4×4×4 and 4×4×3 *q*-points MP meshes have been adopted for a cubic and tetragonal systems respectively.

Results and discussion

The analysis of possible phases of II-VI semiconductors ternary alloys from the material project database [15], led us to identify three new phases for $Mg_xCd_{1-x}O$ compound. In the previous work, the stability of Mg_3CdO_4 (i.e., x=0.75, cubic phase, Pm-3m space group) is confirmed together with its optoelectronic and mechanical properties [5]. The table 1 illustrate the structural parameters of the studied system. As shown in table 1, the parameters for MgO and CdO are in a good agreement with experimental results. The formation enthalpy for ternary alloy $A_xB_{1-x}C$ is defined by equation 1, as:

$$\Delta H = E(A_xB_{1-x}C)\text{-}x\ E(A) - (1\text{-}x)\ E(B)\ \text{-}E(C) / y \qquad \text{(eq.1)}$$

Where $E(A_xB_{1-x}C)$ is the total energy of the alloy at composition x. E(A), E(B) and, E(C) are the total energies of elements that form the alloy optimized in their bulk structure, and y is the number of atoms of the compound. The calculated ΔH (x=0.25) and, ΔH (x=0.50) are -1.36 eV/atm and -1.78 eV/atm respectively; indicating that this alloy may be thermodynamically stable.

The elastic constants are depicted in table 2, representing a local stability according to Born stability criteria [16], given by equation 2 and 3 for cubic and tetragonal systems respectively. Further, the phonon dispersion spectrums were calculated and represented in figure 2. the results show no imaginary frequencies for the phases $MgCd_3O_4$ (P-43m), $MgCdO_2$ (P/mmm) and for, Mg_3CdO_4 (Pm-3m) it has been reported previously [5], indicating a dynamic stability of the system in the studied new phases. It is Noteworthy, that $MgCd_3O_4$ is not stable in Pm-3m space group and we have not tested the stability of Mg_3CdO_4 in the space group P-43m.

$$C_{11}+2C_{12}>0,\ C_{11}-C_{12}>0,\ C_{44}>0 \qquad \text{(eq.2)}$$

$$C_{11}>|C_{12}|,\ 2C_{13}^2<C_{33}(C_{11}+C_{12}),\ C_{44}>0,\ C_{66}>0 \qquad \text{(eq.3)}$$

Beside the structural stability, understanding the elastic properties can predict the behavior of materials (i.e. stiffness, ductile or brittle behavior…), during elaboration under experimental conditions. Moreover, the lattice mismatch between the substrate and the deposited semi-conductor as a thin film can evince stresses on it and affect its properties. The Cadmium Oxide (CdO) is fragile compared with Magnesium Oxide (MgO); therefore, the addition of Mg atoms to CdO can improve its resistance against tensile or attraction and shear deformations. As it can be seen, for 25 % of Mg we observe a slight decrease of the elastic constants. Otherwise, for the rest of the atomic fraction; the stiffness viz the elastic constants increase and the results are listed in table 2. The elastic properties such as Bulk modulus B, shear modulus G, Young's modulus E and Poison's ratio υ, can be estimated using the Voigt-Reuss-Hill approximation [17], based on the elastic constants. These properties are calculated and listed in table 3. The bulk modulus concerns the resistance of the material against volume change, Shear modulus G measures the stiffness against shear deformation, and Young's modulus E, represents the ability of a material to deform elastically. The figure 3.a and 3.b, represent the variation of elastic properties and Pugh's ratio with respect to atomic fraction respectively. These quantities increase with the atomic fraction except for 25 % (see figure 3.a),

indicating that Mg atoms arise the stiffness of this alloy, against the deformation. Another important parameter is Pugh's ratio (ratio between bulk and shear modulus B/G), which describe the behavior of a deformed material. This ratio is related to the transition between brittle and ductile character of a solid and it was observed by Pugh in 1954 [18]. The critical value found by Pugh is 1.75. The ratio B/G reflects the hardness of a material. The smaller the ratio B/G is, the bigger the hardness of the material which is classified as brittle and therefore it can change easily its volume. On the other hand, material with a greater B/G is ductile and can be easily distorted. Pugh's ratio indicate that the alloy becomes brittle by adding Mg atoms.

Conclusion

The purpose of this paper, is to find alternatives for the well-known structures of the system $Mg_xCd_{1-x}O$, to modulate its properties and even to widen the elaboration possibilities for the experimental field. Based on density functional theory calculation, the phases $MgCd_3O_4$, $MgCdO_2$, and Mg_3CdO_4 are thermodynamically, locally and dynamically stable. The elastic constants and properties show that adding Mg atoms to the binary compound CdO to form the alloy $Mg_xCd_{1-x}O_4$ can improve its resistance against tensile or attraction and shear deformations, as a result the material becomes brittle

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Table Captions

Table 1: Calculated structural parameters, bulk modulus B, bulk modulus first derivative with respect to pressure B', for the alloy composition.

Table 2: Calculated elastic constants Cij for $Mg_xCd_{1-x}O$ alloy (x=0,0.25,0.50,0.75 and 1)

Table 3: Calculated bulk modulus B, Young's modulus E, shear modulus G, Poisson's ratio ν and B/G.

Figure Captions

Figure 1: Crystal structures of $Mg_xCd_{1-x}O$ alloy. (a) CdO, (b) MgO, (c) $MgCd_3O_4$, (d) $MgCdO_2$, I Mg_3CdO_4.

Figure 2: Phonon band structure and phonon density of states (PDOS) of (a) $MgCd_3O_4$ and, (b) $MgCdO_2$.

Figure 3: Calculated (a) elastic properties (b) Pugh's ratio, with respect to the atomic fraction of Mg.

Table 1

Atomic fraction **x (%)**	**Structural formula**	**Space group**	**a (Å)**	**c (Å)**	**B (Gpa)**	**B'**
0	**CdO**	**Fm-3m**	4.7706 [a]	-	128.1663 [a]	4.7580 [a]
			4.7774 [b]		125.6225 [b]	4.8920 [b]
			4.7700 [c]		147.0000 [c]	4.2000 [c]
			4.7700 [e]		130.0000 [e]	4.1000 [e]
			4.7790 [h]		141.0000 [h]	4.0000 [h]
25	**$MgCd_3O_4$**	**P-43m**	5.0610 [a]	-	96.3165 [a]	4.7543 [a]
			5.0064 [b]		96.9986 [b]	4.5030 [b]
50	**$MgCdO_2$**	**P4/mmm**	3.2358 [a]	4.5775 [a]	138.2876 [a]	4.8264 [a]
			3.2402 [b]	4.5797 [b]	134.8346 [b]	4.5380 [b]
75	**Mg_3CdO_4**	**Pm-3m**	4.4457 [a]	-	142.2620 [a]	4.4960 [a]
			4.4442 [b]		141.3254 [b]	4.392 [b]
100	**MgO**	**Fm-3m**	4.2584 [a]	-	149.2165 [a]	4.1323 [a]
			4.2541 [b]		149.2977 [b]	4.0230 [b]
			4.2540 [c]		148.6000 [c]	4.3000 [c]
			4.2130 [d]		160.0000 [d]	-
			4.2410 [k]		167.0000 [k]	4.0000 [k]

[a] Wien2k (present work); [b] Quantum Espresso (present work); [c] Reference [19]; [d] Reference [20] ; [e] Reference [21] ;[k] Reference [22] ; [h] Reference [23]

Table 2

x (%)	Formule structurale	Space group	C11(Gpa)	C12(Gpa)	C44(Gpa)	C13(Gpa)	C33(Gpa)	C66(Gpa)
0	CdO	Fm-3m	185.5429 [a] 177.5764 [b] 207.8000 [f] 183.9900 [i]	101.8226 [a] 102.3213 [b] 106.3000 [f] 96.0100 [i]	51.4961 [a] 47.6761 [b] 54.9000 [f] 45.7800 [i]	-	-	-
25	$MgCd_3O_4$	P-43m	103.9901 [a] 116.0914 [b]	72.3860 [a] 89.14168 [b]	41.4389 [a] 39.5041 [b]	-	-	-
50	$MgCdO_2$	P4/mmm	235.9515 [a] 230.7819 [b]	84.9635 [a] 74.2087 [b]	70.2718 [a] 71.9990 [b]	96.6058 [a] 97.0285 [b]	209.9226 [a] 211.8841 [b]	47.7310 [a] 52.8634 [b]
75	Mg_3CdO_4	Pm-3m	248.844 [a] 226.3066 [b]	111.838 [a] 101.6665 [b]	102.618 [a] 96.9935 [b]	-	-	-
100	MgO	Fm-3m	285.2970 [a] 273.8164 [b] 291.0000 [g] 297.0000 [k]	82.8500 [a] 89.3129 [b] 91.0000 [g] 99.6000 [k]	147.1126 [a] 141.9353 [b] 139.0000 [g] 151.9000 [k]	-	-	-

[a] Wien2k (present work); [b] Quantum Espresso (present work); [f] Reference [24] ; [g] Reference [25]; [i] Reference [26]; [k]Reference [22]

Table 3

x (%)	Structural formula	Space group	B (Gpa)	E (Gpa)	G (Gpa)	υ	A	B/G
0	CdO	Fm-3m	129.7290 [a] 127.4063 [b]	126.7540 [a] 116.8403 [b]	47.3970 [a] 43.3657 [b]	0.3370 [a] 0.3471 [b]	1.2302 [a] 1.2671 [b]	2.7370 [a] 2.9379 [b]
25	$MgCd_3O_4$	P-43m	82.9207 [a] 98.1249 [b]	75.8028 [a] 70.7889 [b]	28.1573 [a] 25.6887 [b]	0.3461 [a] 0.3778 [b]	2.6224 [a] 2.9317 [b]	2.9449 [a] 3.8198 [b]
50	$MgCdO_2$	P4/mmm	137.5090 [a] 134.4371 [b]	165.5060 [a] 169.3200 [b]	63.6860 [a] 65.6246 [b]	0.2990 [a] 0.2900 [b]	1.1125 [a] 1.1584 [b]	2.1592 [a] 2.0486 [b]
75	Mg_3CdO_4	Pm-3m	142.2620 [a] 143.2132 [b]	220.9990 [a] 204.9288 [b]	87.2720 [a] 81.2305 [b]	0.2660 [a] 0.2614 [b]	1.4980 [a] 1.5564 [b]	1.8048 [a] 1.7630 [b]
100	MgO	Fm-3m	150.332 [a] 150.8141 [b] 155.0000 [h] 165.5000 [k]	296.632 [a] 283.4230 [b] 249.0000 [h] 305.0000 [k]	126.643 [a] 119.4200 [b] 155.0000 [h] 127.9000 [k]	0.1710 [a] 0.1866 [b] 0.1800 [h] 0.2520 [k]	1.4533 [a] 1.5386 [b] - 0.7600 [k]	1.1870 [a] 1.2629 [b] - -

[a] Wien2k (present work); [b] Quauntum Espresso (present work); [h] Reference [27];[k] Reference [22];[f] Reference [23]

Figure 1

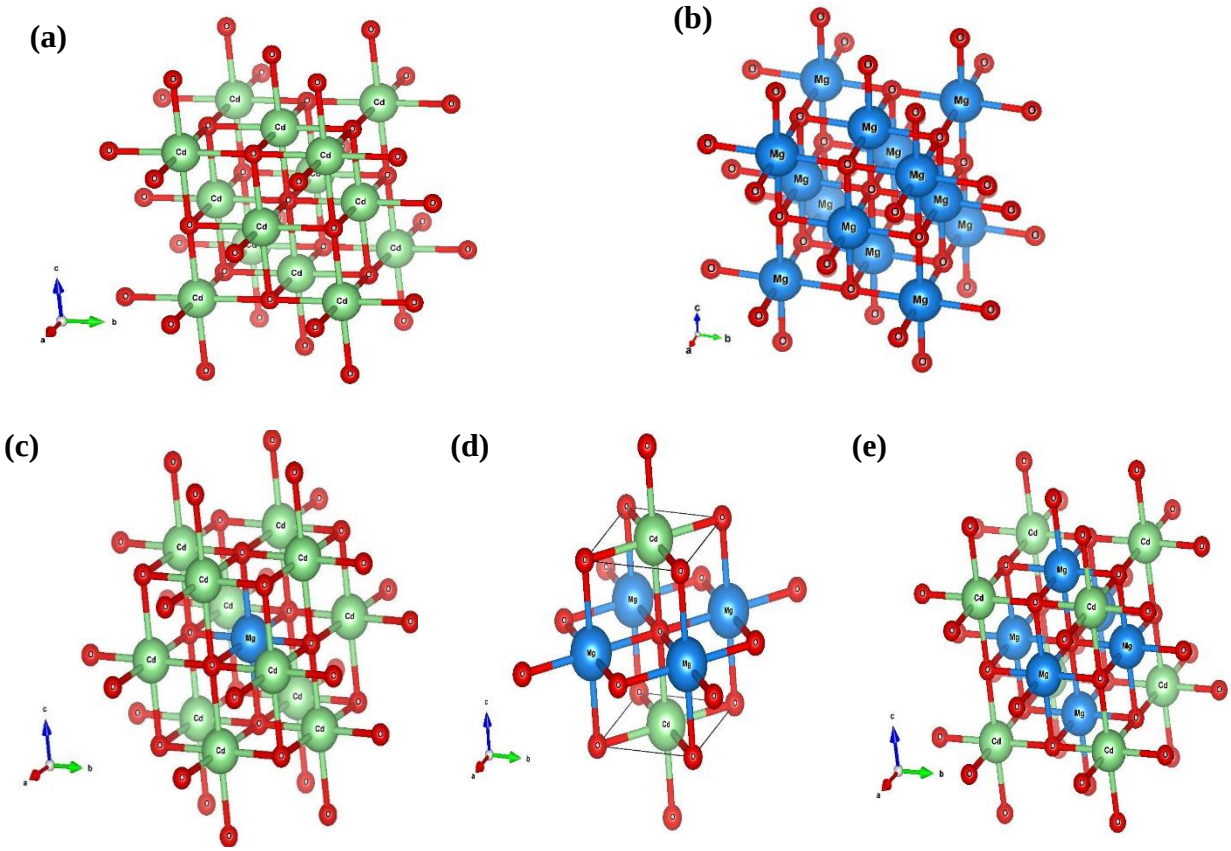


Figure 2

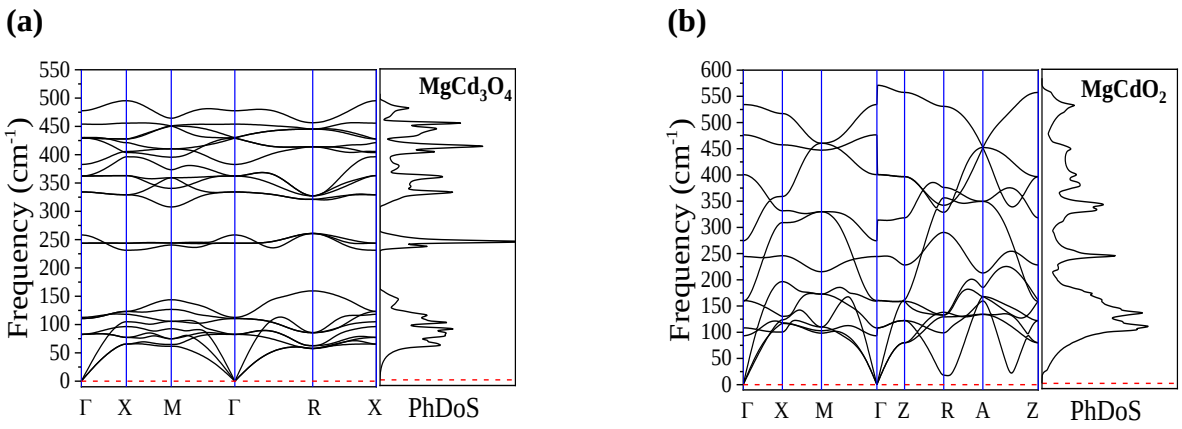
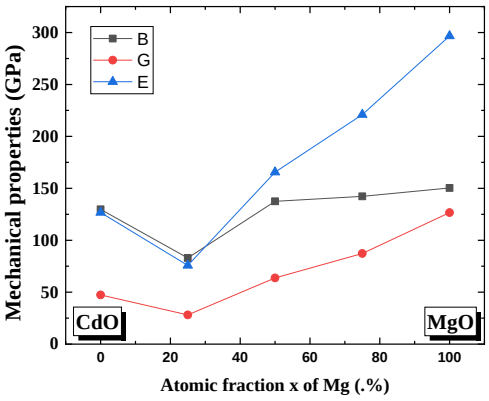
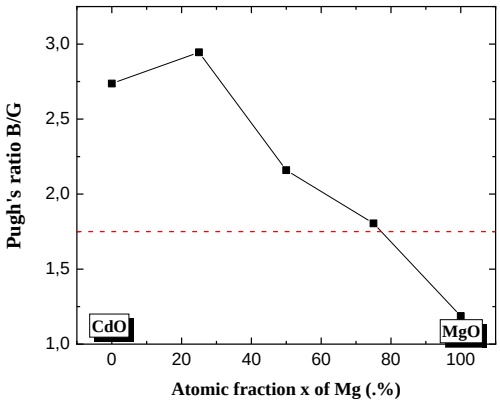


Figure 3

(a)


B
G
E
Mechanical properties (GPa)
300
250
200
150
100
50
0
CdO
MgO
0
20
40
60
80
100
Atomic fraction x of Mg (.%)

(b)


Pugh's ratio B/G
3,0
2,5
2,0
1,5
1,0
CdO
MgO
0
20
40
60
80
100
Atomic fraction x of Mg (.%)