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First Principles Study of the Structural, Elastic, Electronic and Phonon Properties of CdX_2O_4 (X=Al, Ga, In) Spinel-Type Oxides

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Abstract. We have performed *ab-initio* calculations of the structural, electronic, elastic and dynamical properties for the spinel compounds CdX_2O_4 (X=Al, Ga, In) using the plane wave pseudo-potential method within the generalized gradient approximation (GGA). The calculated lattice parameters, elastic constants for these compounds are in good agreement with the previous calculated values. The computed direct band gaps of $CdAl_2O_4$, $CdGa_2O_4$ and $CdIn_2O_4$ are 2.90 eV, 1.92 eV and 1.16 eV, respectively. The lattice vibrations were calculated by direct method. The calculated phonon dispersion curves show that all compounds are dynamically stable in the spinel structure.

Keywords: Spinel oxides, band gap, elastic constants, phonon dispersion curves.
PACS: 71.15.-Mb, 63.20.D, 62.20.de, 63.20.dk.

INTRODUCTION

CdX_2O_4 (X=Al, Ga, In) are members of the class of inorganic materials called spinel oxides. Spinel oxides CdX_2O_4 (X=Al, Ga, In) have a closed-packed face-centred-cubic structure, with space group Fd-3m (#227) and its unit cell contains eight CdX_2O_4 molecules [1]. They are characterized by several desirable properties, e.g. a high melting point, high reflectivity, high strength, chemical resistivity at elevated temperatures and low electrical loss [2, 3]. CdX_2O_4 (X=Al, Ga, In) spinel compounds have been a subject of many experimental and theoretical works, focusing on the structural [4–8], electronic [4, 7-10] and optical properties [4, 7-9, 11]. Although considerable progress has been made in theoretically and experimentally describing the structural, electronic, optical and elastic properties of CdX_2O_4 (X=Al, Ga, In) compounds, many of their phonon properties are still not well established. This article is organized as follows Sec. 2 briefly describes the method. In section 3, we discuss the calculated structural parameter (3.1), electronic band structure and partial density of states (3.2), second order elastic constants (3.3) and phonon spectrum (3.4).

CALCULATIONAL DETAILS

The *ab initio* calculations were performed with the density functional theory, using the MedeA–Vasp package [12, 13] with the projector augmented wave potential [14] construction. For the exchange-correlation functional, the generalized gradient approximation [15] of Perdew–Burke–Ernzerhof [16] was taken. According to a careful checking the convergence of total energy with respect to the energy cut off of plane wave and the size of k-mesh, we adopted a plane-wave basis set with the cut off energy of 400 eV in all calculations. In the **k**-points sampling routine, Brillion-zone integrations were using the special k-points sampling of Monhkorst–Pack [17] scheme with 3×3×3. The phonon dispersion curves based on the direct method [18], in which the forces are calculated via the Hellmann-Feynman theorem have been investigated for CdX_2O_4 (X=Al, Ga, In).

RESULTS AND DISCUSSION

Structural Properties

Spinel oxides CdX_2O_4 (X=Al, Ga, In) have a closed-packed face-centred-cubic structure, with space group Fd-3m (#227) and its unit cell contains eight CdX_2O_4 molecules [19]. The unit-cell of the cubic spinel CdX_2O_4 contains 56 atoms; 8 Cd cations, 16 X cations and 32 O anions. The positions of the cations Cd and X are fixed by the

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symmetry, but the anion O positions are variable and are specified by the anion parameter u. Cd cations occupy the Wyckoff position 8a (0.125, 0.125, 0.125), X cations are located at the Wyckoff position16d (0.5, 0.5, 0.5) and O anions are positioned at the Wyckoff position 32e (u, u, u). Then its crystal structure is characterized by two parameters: the lattice constant a_0 and the internal anion parameter u. The calculated structural parameters of CdX_2O_4 (X=Al, Ga, In) are summarized in Table 1. Results from earlier experimental and theoretical works are quoted for comparison.

TABLE 1. The parameters of the ground-state structures (a_0 (in Å) and u), bulk modulus B_0 (in GPa),the elastic constants (C_{11} ,C_{12}, C_{44} (in GPa)) for $CdAl_2O_4$, $CdGa_2O_4$ and $CdIn_2O_4$ spinel compounds.

Compounds	*Reference*	a_0 (Å)	*u*	B_0 (GPa)	C_{11} (GPa)	C_{12} (GPa)	C_{44} (GPa)
$CdAl_2O_4$	Present	8.3767	0.27009	203.42	309.03	150.61	146.41
	[6]	8.0780	-	-	-	-	-
	[5]	8.3816	0.2714	180	231	149	115
	[20]	8.3844	0.2697	187	292	134	78
	[21]	8.355	-	-	-	-	-
	[22]	8.33	-	-	-	-	-
$CdGa_2O_4$	Present	8.6232	0.26748	190.69	277.25	147.40	113.55
	[6]	8.579	-	-	-	-	-
	[5]	8.7327	0.2683	158	203	130	91
	[23]	8.602	-	-	-	-	-
	[24]	8.759	0.2682	166.68	-	-	-
$CdIn_2O_4$	Present	9.1864	0.26190	158.36	257.90	108.59	72.96
	[6]	9.13	0.262	-	-	-	-
	[5]	9.3631	0.2630	126	159	102	57
	[23]	9.1651	0.2627	-	-	-	-
	[24]	9.330	0.2631	135.05	-	-	-

Electronic Structure

The calculated electronic band structure for the spinel $CdAl_2O_4$, $CdGa_2O_4$ and $CdIn_2O_4$ oxides calculated along the high symmetry directions is shown in Fig. 1. All the three spinels have an indirect band gap. The overall band profiles are in fairly good agreement with previous theoretical results, using FPLAW method [24]. The valence band maximum (VBM) is located at Γ point for $CdAl_2O_4$ and at K point for $CdAl_2O_4$, $CdIn_2O_4$, whereas the conduction band minimum (CBM) is located at Γ point for all three compounds, making these three compounds to be an indirect gap materials. In these compounds the top of the valence band (VBM) and the bottom of the conduction band (CBM) are found to be at Γ point resulting in a direct band gap insulator (Γ – Γ) of about 2.90 eV, 1.92 eV and 1.16 eV for $CdAl_2O_4$, $CdGa_2O_4$ and $CdIn_2O_4$, respectively. Table 2 shows our calculated values of the direct band gaps and indirect band gaps for $CdAl_2O_4$, $CdGa_2O_4$ and $CdIn_2O_4$ spinel compounds.

TABLE 2. Some direct band gaps (Γ-Γ, L-L, X-X, K-K and W-W) and indirect band gaps (Γ-L, Γ-X, Γ-K and Γ-W) for $CdAl_2O_4$, $CdGa_2O_4$ and $CdIn_2O_4$ compounds. All energies are in eV.

Materials	*References*	*Γ-Γ*	*L-L*	*X-X*	*K-K*	*W-W*	*Γ-L*	*Γ-X*	*Γ-K*	*Γ-W*
$CdAl_2O_4$	This study	2.90	5.34	6.03	5.88	6.36	5.08	5.69	5.66	5.78
	[GGA-20]	2.76	5.207	5.968	-	-	3.031	3.123	-	-
	[GGA-EV-20]	3.669	5.952	6.720	-	-	3.907	4.010	-	-
$CdGa_2O_4$	This study	1.92	4.70	5.48	5.50	5.86	4.72	5.44	5.61	5.81
	[GGA-24]	1.976	4.759	5.472	5.470	5.874	1.984	-	1.899	-
	[GGA-EV-24]	2.765	5.500	6.111	6.216	6.639	2.837	-	2.736	-
$CdIn_2O_4$	This study	1.16	3.80	4.68	4.83	5.22	3.84	4.67	4.90	5.11
	[GGA-24]	1.174	3.840	4.725	4.848	5.148	1.104	-	1.127	-
	[GGA-EV-24]	2.133	4.604	5.429	5.571	5.898	2.032	-	2.020	-

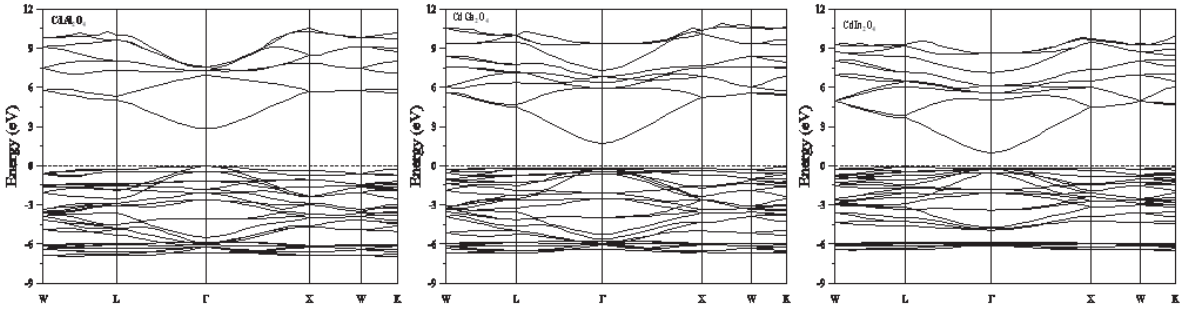

FIGURE 1. Band structure along the principal high symmetry directions in the Bz for $CdAl_2O_4$, $CdGa_2O_4$ and $CdIn_2O_4$ compounds.

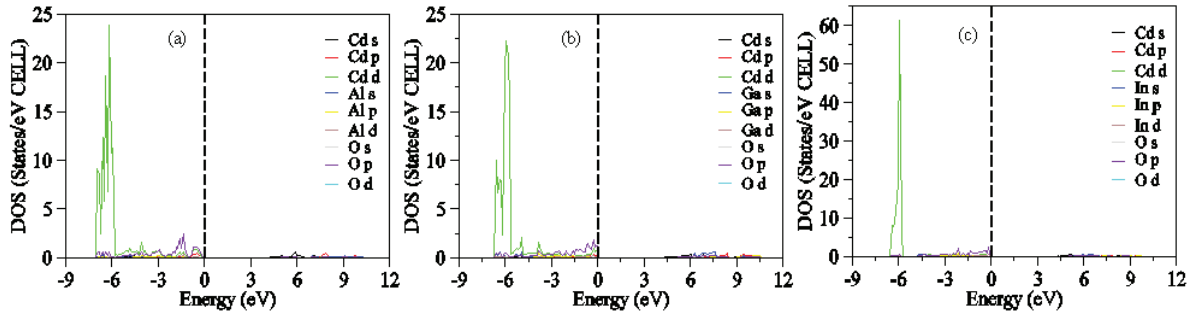

FIGURE 2. Partial DOS for $CdAl_2O_4$ (a), $CdGa_2O_4$ (b) and $CdIn_2O_4$ (c) compounds.

Elastic Properties

Elastic constants are significant parameters of a material, and often provide valuable information on the structural stability. A cubic system has three independent elastic constants C_{11}, C_{12}, C_{44}. The calculated values for *B, C_{11}, C_{12}, C_{44}* for $CdAl_2O_4$, $CdGa_2O_4$ and $CdIn_2O_4$ are listed in Table 1. Our results have been compared with the available theoretical and experimental results in this table. Our calculated values of *B, C_{11}, C_{12}, C_{44}* have been found to be higher than the previous theoretical results for all three materials [5, 20, 24].

Phonon Properties

In Fig. 3, we have plotted the phonon dispersion curves of CdX_2O_4 (X=Al, Ga, In) compounds in the spinel structure. The phonon properties of CdX_2O_4 (X=Al, Ga, In) compounds are calculated within the generalized gradient approximation (GGA) in the spinel structure, with space group symmetry Fd-3m (#227). The calculated phonon dispersion curves of CdX_2O_4 (X=Al, Ga, In) confirm that three compounds are dynamically stable in the spinel structure without any imaginary phonon frequencies. The phonon properties of CdX_2O_4 (X=Al, Ga, In) compounds have not yet been calculated. Then our results can provide reference data for next investigations.

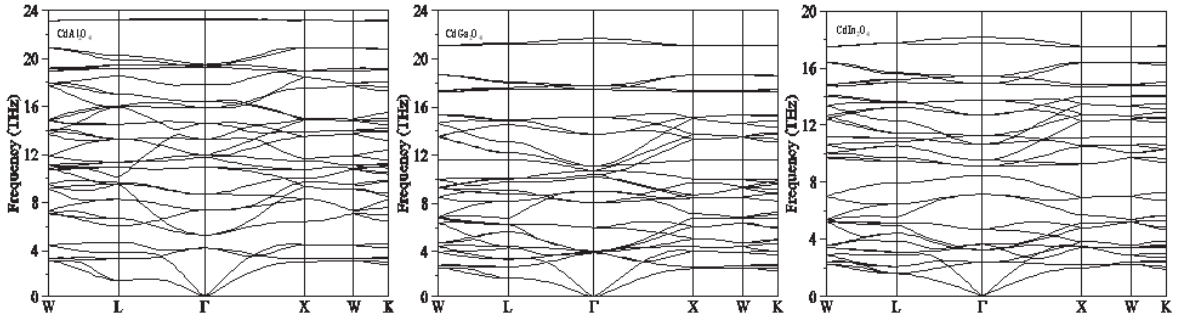

FIGURE 3. Calculated phonon dispersion curves for CdX_2O_4 (X=Al, Ga, In) compounds along lines of high symmetry in the Brillouin zone.

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