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Structural, Elastic, Electronic and Phonon Properties of SnX_2O_4 (X=Mg, Zn, Cd) Spinel from Density Functional Theory

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Abstract. First-principle calculations of structural, electronic, elastic and phonon properties of $SnMg_2O_4$, $SnZn_2O_4$ and $SnCd_2O_4$ compounds are presented, using the pseudo-potential plane waves approach based on density functional theory (DFT) within the generalized gradient approximation (GGA). The computed ground state structural parameters, i.e. lattice constants, internal free parameter and bulk modulus are in good agreement with the available theoretical results. Our calculated elastic constants are indicative of stability of SnX_2O_4 (X=Mg, Zn, Cd) compounds in the spinel structure. The partial density of states (PDOS) of these compounds is in good agreement with the earlier ab-initio calculations. The phonon dispersion relations were calculated using the direct method. Phonon dispersion results indicate that $SnZn_2O_4$ is dynamically stable, while $SnMg_2O_4$ and $SnCd_2O_4$ are unstable.

Keywords: Electronic band structure, elastic properties, dynamical properties.
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INTRODUCTION

A large group of compounds with spinel structure are generally described by the AB_2X_4 formula, where A and B are metals in oxidation states II-III or II-IV (II= Cd, Mg, Zn; III= Al, Ga, In and IV= Si, Ge, Sn), and X is a divalent anion. These compounds have been a subject of many experimental and theoretical works [1-7]. Experimentally, these compounds have been synthesized using many elaboration methods, such as thermal evaporation, high temperature calcinations, sol–gel synthesis, ball-milling and rf magnetron sputtering [1, 2]. Allali et. al. [1] performed a theoretical study on elastic and thermodynamic properties of $SnMg_2O_4$, $SnZn_2O_4$, $SnCd_2O_4$ spinel oxides. Electronic band structure optical response of spinel SnX_2O_4 (X=Mg, Zn) were calculated using full potential linearized augmented plane-wave with the mixed basis FP-LAPW+lo method by Manzar et. al. [2]. The theoretical results of the structural, elastic, electronic and optical properties of spinel $SnMg_2O_4$ compound have been presented by Reffas [3].

CALCULATIONAL DETAILS

All the calculations have been performed using the plane-wave pseudo-potential DFT method implemented in the MedeA-VASP package [8, 9]. Projector Augmented Wave (PAW) pseudo-potentials were used to present the ionic potentials. The Perdew–Burke–Ernzerhof (PBE) [10] exchange-correlation functional was treated at the generalized gradient approximation (GGA). In fact, the calculated results of GGA (PAW-PBE) are in reasonable agreement with the experimental values in all cases, this shows that the pseudo-potential and our methods are suitable for this study. 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, the plane-wave basis set energy cutoff was set at 400 eV in all calculations. The Monkhorst-Pack [11] scheme k-points grid sampling was set at 3× 3 × 3 for the Brillouin zone. The Fermi distribution function with a smearing parameter of 0.2 eV was used to integrate the bands at Fermi level. Phonon dispersion curves are calculated using the MedeA-PHONON [12] module with the forces calculated with the Vasp.

RESULTS AND DISCUSSION

SnX_2O_4 (X=Mg, Zn and Cd) adopt the normal spinel structure (space group Fd-3m). They are characterized by the lattice parameter a_0 and an internal parameter u. The Sn atoms are located at the Wyckoff positions 8a (1/8, 1/8,

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1/8) tetrahedral sites, whereas Mg, Zn and Cd atoms are located at the 16d (1/2, 1/2, 1/2) octahedral sites and the O atoms at 32e (*u, u, u*) of the face centered cubic structure.

The calculated equilibrium lattice parameters, including the lattice constant a_0, internal structural parameter u, Bulk modulus *B*, Shear modulus *G* and *B*/*G* ratio was calculated, we are summarized and compared with available other data in Table 1. The present calculated ground-state properties are in good agreement with the available theoretical results [1, 3, 4, 7]. The elastic constants require knowledge of the derivative of the energy as a function of lattice strain. In the case of cubic system, there are only three independent elastic constants, namely, C_{11}, C_{12} and C_{44}. The calculated values of elastic constants are listed in Table 1. According to Pugh [13], if *B*/*G* ratio is smaller than 1.75, the material behaves in a brittle manner; other-wise, the material behaves in a ductile manner. It is clearly seen from Table 1 that $SnZn_2O_4$ and $SnCd_2O_4$ are ductile materials; however, $SnMg_2O_4$ is brittle.

TABLE 1. Calculated lattice constant a_0 , internal structure parameters *u*, Bulk modulus *B* (in GPa), elastic constants (C_{11} ,C_{12} and C_{44}, (in GPa)), Shear moduli *G* (in GPa) and *B*/*G* ratio.

Compounds	*Reference*	a_0 (Å)	*u*	*B (GPa)*	C_{11} (GPa)	C_{12} (GPa)	C_{44} (GPa)	*G* (GPa)	*B/G*
$SnMg_2O_4$	Present	8.5902	0.25786	163.46	254.19	118.10	126.70	98.72	1.66
	[1]	8.5181	0.2584	186.51	289.04	135.24	75.40	75.99	2.45
	[3-LDA]	8.525	0.2569	163.98	228	132	102	75.4	2.17
	[3-GGA]	8.777	0.2582	133.58	180	107	90	62.7	2.10
	[4-LDA]	8.557	0.2569	182.92	-	-	-	-	-
	[4-GGA]	8.709	0.2557	151.48	-	-	-	-	-
	[5-LDA]	8.671	0.2551	160.57	-	-	-	-	-
	[5-GGA]	8.845	0.2618	139.11	-	-	-	-	-
	[7]	8.6000	0.3750	-	-	-	-	-	-
$SnZn_2O_4$	Present	8.5979	0.25827	199.27	254.81	171.50	115.27	76.68	2.59
	[1]	8.5517	0.2580	191.16	250.75	161.36	42.74	43.51	4.39
	[4-LDA]	8.569	0.2574	191.78	-	-	-	-	-
	[4-GGA]	8.785	0.2555	150.95	-	-	-	-	-
	[7]	8.6574	0.3900	-	-	-	-	-	-
$SnCd_2O_4$	Present	9.0588	0.25121	184.34	260.68	146.17	77.51	68.65	2.68
	[1]	9.0841	0.2507	161.50	227.10	128.69	48.55	48.81	3.31
	[4-LDA]	9.112	0.2491	161.87	-	-	-	-	-
	[4-GGA]	8.6310	0.2502	124.19	-	-	-	-	-
	[7]	9.1430	0.3920	-	-	-	-	-	-

We present the partial densities of states for $SnMg_2O_4$, $SnZn_2O_4$ and $SnCd_2O_4$ along high-symmetry directions in the Brillouin zone, as presented in Fig. 1. Accordingly, the spinel oxides are predicted to be direct gap materials. Both the top of the valence band and the bottom of the conduction band are found to be at Γ. The computed direct band gaps of $SnMg_2O_4$, $SnZn_2O_4$, $SnCd_2O_4$ are 2.07 eV, 0.49 eV and 0.29 eV, respectively. The calculated electronic band structures for $SnMg_2O_4$, $SnZn_2O_4$, $SnCd_2O_4$ are shown in Fig. 2. The calculations were performed using GGA with the relaxed atomic positions. The scale of energy in all figures is in eV and the top of the valence band is set to zero (Fermi level) on the energy scale.

In Fig. 3, the calculated phonon dispersion curves are shown along several high-symmetry lines in the Brillouin Zone. The phonon spectra of $SnZn_2O_4$ show that these compounds are dynamically stable without any imaginary

phonon modes. On the contrary, we find imaginary phonon frequency in the L symmetry point for $SnMg_2O_4$ and $SnCd_2O_4$. Allali *et al.* [1] calculated phonon frequencies by using CASTEP program. In this study Allali *et al.* found that all three compounds are dynamically stable without any imaginary phonon modes [1].

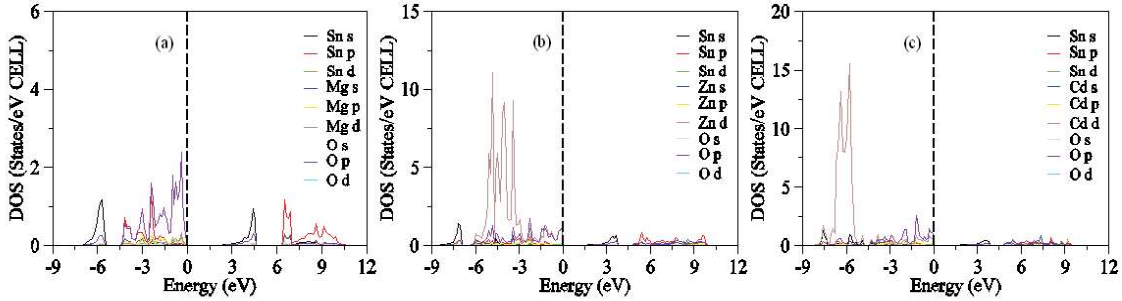

FIGURE 1. Partial densities of states for $SnMg_2O_4$, $SnZn_2O_4$, $SnCd_2O_4$ spinel compounds.

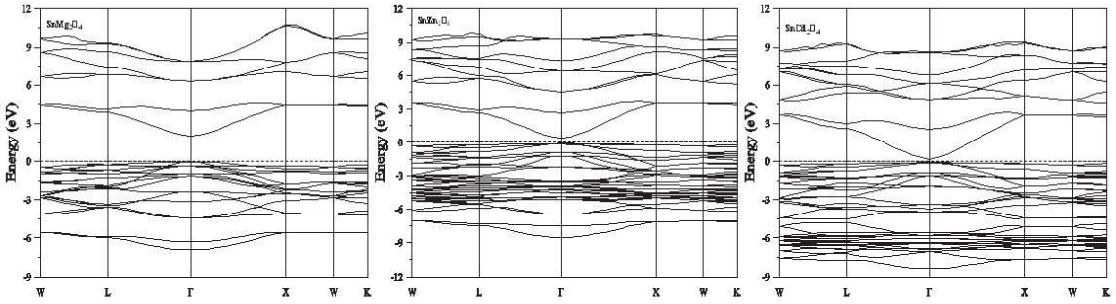

FIGURE 2. Calculated electronic band structures for $SnMg_2O_4$, $SnZn_2O_4$, $SnCd_2O_4$ spinel compounds.

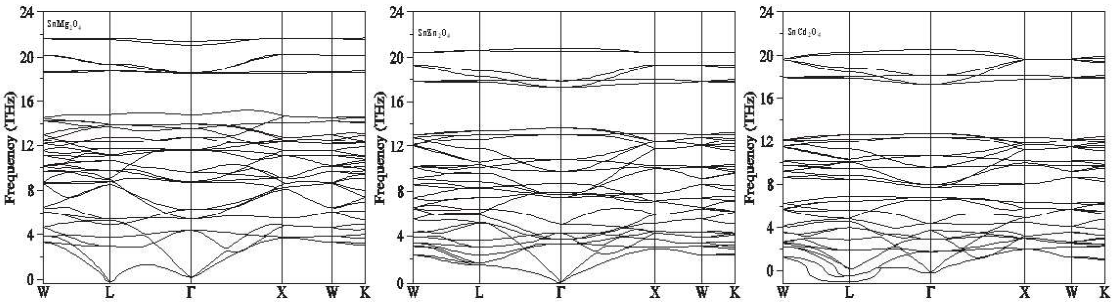

FIGURE 3. Calculated phonon dispersion curves for $SnMg_2O_4$, $SnZn_2O_4$, $SnCd_2O_4$ spinel compounds along several lines of high symmetry in the Brillouin zone.

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