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Structural, electronic, elastic, optical and vibrational properties of MAl_2O_4 (M = Co and Mn) aluminate spinels

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ABSTRACT

First principles density functional theory calculations were performed to study structural, electronic, elastic, optical and vibrational properties of $CoAl_2O_4$ and $MnAl_2O_4$ aluminate spinels. Computed ground state properties such as unit-cell parameter and oxygen positional parameter differ by less than 1% from previously available theoretical and experimental results. However, the bulk modulus differs by less than 4% difference from available theoretical and experimental values for $CoAl_2O_4$ and less than 10% for $MnAl_2O_4$. Zone-center phonon frequencies and the phonon spectrum along high symmetry direction together with the phonon density of states were calculated using supercell method. Bandgaps of $CoAl_2O_4$ and $MnAl_2O_4$ were obtained as 1.78 and 2.21 eV respectively. $CoAl_2O_4$ was found to be more ionic than the $MnAl_2O_4$ spinel. And quasi harmonic method was used to calculate the Debye temperature for the studied compounds.

1. Introduction

In recent solar cell technologies, the photoelectrochemical (PEC) process is used to store energy and produce renewable energy. The PEC process uses sun light to generate the hydrogen from water and produce chemical energy carrier. In 1970s, the large band gap ~ 3 eV semiconductor TiO_2 [1] was used for PEC but this semiconductor was only used to absorb UV rays of sunlight, but unfortunately only about 5% of absorbed sunlight was useful [2]. Therefore, over the last forty years, it has become a great challenge for material scientists to discover a low cost, more stable and efficient semiconductor which generates more electrons and holes with sunlight. However, current metal oxides are not sufficient to obtain sustained efficiency in energy applications. Therefore, it is still a hot research area for scientists to look for new lower band gap materials that can potentially absorb visible light and exhibit reasonable PEC properties. Among various metal oxides, spinels are very promising especially for PEC. Co-Fe-Al oxide spinel system having optical band gaps between 1.6 and 2.0 eV is a good candidate for PEC applications [3–6]. Recently, Woodhouse et al. showed that the spinel oxide $CoAl_2O_4$ is a good material for PEC process [7,8]. The $CoAl_2O_4$ is already used for the ceramic pigmentation [9,10], optical coating and catalyst for the reformation of methane [11]. It is also used for the coloration of plastics, paint, fibers, paper, rubber, glass and cement due to its thermal and chemical stability [12]. Moreover, most of the ceramic dyeing materials used in pigment industries are made of transition metal oxides with the spinel structure, as they guarantee high surface area, thermal stability and chemical resistance [13,14]. More generally, spinels with different transition metals are potential candidates for several modern technological applications, such as high density magnetic recording, microwave devices, magnetic fluids, heterogeneous catalysis and absorbent materials [15–17].

Due to their many practical applications, physical properties of spinel-based materials have been studied by many researchers either experimentally [18–24] or theoretically [25–27]. Among these latter, Feng et al. [25] calculated the electronic and optical properties of CoX_2O_4 (X = Al, Ga, In) spinels and Tielens et al. [26] calculated structural and electronic properties of $(Co_{1-x}Al_x)[Co_xAl_{2-x}]O_4$ using first principles density functional theory. The combination between experimental and theoretical approach is definitely less frequent. Recently, Walsh et al. [28] have studied the electronic properties of $CoAl_2O_4$ both experimentally and theoretically. Furthermore, aluminate spinels other than $CoAl_2O_4$ have been poorly explored.

Since one of the main objective of researchers is to develop low band gap semiconductors to increase the efficiency of the absorbed sunlight in photoelectrochemical (PEC) process due to the fact that conventional TiO_2 having bandgap of 3 eV can only absorb 5% of the

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absorbed sunlight which is not efficient, we look for different spinel type materials that can be used. In the present study, we have calculated the structural, elastic, electronic, optical and vibrational properties of $CoAl_2O_4$ and $MnAl_2O_4$ spinels using first principles density functional theory calculations. Results obtained are compared with the few data available in the literature for $CoAl_2O_4$ and the very scarce data available for $MnAl_2O_4$ spinels, in order to explore the true potential of these compounds for PEC applications.

2. Computational method

Calculations were done using the DFT approach as implemented in the code MedeA [29,30]. They were performed using the projected augmented wave (PAW) pseudo-potentials [31,32] with the generalized gradient approximation as implemented by Perdew et al. (GGA-PBE) [33]. Electronic correlation effects were considered by using GGA + U with U_{eff} = 2 eV for Co and Mn. The Brillouin zone was integrated using Monkhorst-Pack generated sets of **k**-points [34]. To reach convergence for $CoAl_2O_4$ and $MnAl_2O_4$ spinels, 5 × 5 × 5 and 7 × 7 × 7 **k**-points mesh found to be sufficient, respectively. A kinetic energy cut off 540 eV and a total energy convergence threshold of 10^{-5} eV were used. The elastic properties were calculated using the MT module of MedeA [35]. The direct method (or supercell method) was used to study the phonon properties [36]. As both $CoAl_2O_4$ and $MnAl_2O_4$ are essentially normal spinels [18,21], during the calculations an ordered cation distribution was adopted, with Co and Mn being in tetrahedral coordination and Al in octahedral coordination.

3. Results and discussion

3.1. Structural properties

Aluminate spinels (Co, Mn)Al_2O_4 crystalize in the space group $Fd-3m$, and have face-centered cubic array of oxygen atoms with eight formula per unit cell. Co and Mn occupy the tetrahedrally coordinate sites (8*a* Wyckoff positions) with coordinates (1/8, 1/8, 1/8), while Al occupies the octahedrally coordinate sites (16*d* Wyckoff positions) with coordinates (1/2, 1/2, 1/2). The anion O occupies the 32*e* Wyckoff positions with coordinate (*u*, *u*, *u*) where *u* (0.24–0.27) is usually known as oxygen positional parameter [37]. The calculated equilibrium unit-cell parameter *a* and the *u*-parameter for $CoAl_2O_4$ and $MnAl_2O_4$ are given in Table 1 together with the previous experimental [21,38–40] and theoretical [19,27] results. From Table 1, it is clearly seen that the calculated unit-cell parameter for $CoAl_2O_4$ and $MnAl_2O_4$ are very close to the experimental results. The difference between the obtained lattice parameter values and the experimental values is less than 1%. Although the difference between calculated and experimental *a*-parameter is less than 1%, the real difference is about 0.07 Å which is significantly large in crystal-chemical terms. This shows the limitation of the GGA method in describing the structural parameters. The calculated bulk modulus and the total magnetic moments are also listed in Table 1. Calculated bulk modulus of $CoAl_2O_4$ is 202,70 and experimental value of bulk modulus available in literature for $CoAl_2O_4$ [27] is 210,4. Difference between the present bulk modulus and the experimental ones for $CoAl_2O_4$ is less than 4% percent. For $MnAl_2O_4$, calculated bulk modulus is underestimated compared to the experimental ones, with a difference of about 10%. Compared to experimental data, we observed that GGA overestimates the unit-cell parameter which is consistent with the general trend of these approximations.

Table 1
Calculated lattice parameter a_0 (in Å), internal structure parameters *u*, total magnetic moment (M_{tot}, in μ_B), and bulk modulus $B_V = B_R = B$ (in GPa).

		a_0	*u*	M_{tot}	B
$CoAl_2O_4$	This study	8.17360	0.26430	3.00	202.70
	Exp [18]	8.10470	0.26355		
	Exp [39]	8.10300			210.4
	Theory [27]	8.10559	0.26384		197.3
	Theory [28]	8.19000		2.57	
	Theory [38]	8.10559	0.26384		
$MnAl_2O_4$	This study	8.28350	0.26630	5.00	181.45
	Exp [40]	8.21040	0.26588		200.3
	Exp [21]	8.21040	0.26588		

Table 2
Calculated elastic constants C_{11}, C_{12} and C_{44}, shear modulus G, Young's modulus E in GPa, for $CoAl_2O_4$ and $MnAl_2O_4$.

		C_{11}	C_{12}	C_{44}	G_V	G_R	G	E
$CoAl_2O_4$	This study	269.25	169.43	128.35	96.97	78.81	87.89	230.10
	Exp. [39]	290.5	170.3	138.6			99.1	256.8
$MnAl_2O_4$	This study	248.31	148.02	108.01	84.87	73.90	79.35	207.73
	Exp. [40]	271.3	164.8	124.9			88.7	231.9

3.2. Elastic properties

The elastic constant reveals the response of the materials with the externally applied stress. The elastic constants of a material can be calculated using first principles method by knowing the total energy at appropriate deformation of crystals. Cubic crystals have three elastic constants C_{11}, C_{12} and C_{44}. The calculated elastic constants for $CoAl_2O_4$ and $MnAl_2O_4$, together with their experimental values available in literature [33], are listed in Table 2. The latter shows that the studied spinels satisfy. Table 2 shows that the studied compound satisfies the generalized stability criteria of cubic crystal [41]

$$(C_{11} - C_{12}) > 0,\ C_{12} < B < C_{11},\ (C_{11} + 2C_{12}) > 0,\ C_{44} > 0 \quad (1)$$

Elastic constant C_{11} represents the resistance in x-direction against the linear compression [42,43]. Elastic constant C_{11} is greater than the C_{12} and C_{44} for (Co, Mn)Al_2O_4, showing that these compounds are less compressible along the x-direction. We have also calculated Young's modulus E and shear modulus G using Voigt–Reuss–Hill (VRH) method [44–46], Poisson's ratios are tabulated in Table 2 together with the experimental results [39,40]. Therefore, we can conclude that the present elastic constants are consistent with the experimental ones.

The ductility or brittleness of a material can be determined by Pugh's ratio B/G [47,48] which is accepted as the most reliable criteria. If the value of B/G ratio is greater than 1.75 then the material is ductile and if the ratio B/G is less than 1.75 then the material is brittle in nature. The value of B/G is 2.306 and 2.287 for $CoAl_2O_4$ and $MnAl_2O_4$ respectively, and these values show that these compounds are ductile in nature. The Cauchy pressure (C_{11}-C_{44}) is the classical criteria to determine the ductile or brittle nature of the material. The positive or negative value of Cauchy pressure shows that the material is ductile or brittle in nature [45,49,50]. In the present study, the Cauchy pressure is found to be positive hence the studied compounds confirmed to be ductile in nature.

Acoustic sound velocities and Debye temperature are also calculated using the calculated elastic constants of $CoAl_2O_4$ and $MnAl_2O_4$ and are listed in Table 3 along with the available previous experimental results. The expressions for the calculations are given elsewhere [51].

3.3. Electronic properties

We have calculated the spin up and spin down band structure together with the total density of states for $CoAl_2O_4$ and $MnAl_2O_4$ along high symmetry directions as shown in Fig. 1(a) and (b) respectively. Fig. 1(a) and (b) show that the studied compounds are direct band gap semiconductors with band gaps of 1.78 eV and 2.21 eV for $CoAl_2O_4$ and