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Electronic and structural properties of NaZnAs compound; an ab-initio study in the tetragonal and cubic α phases

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Abstract

A theoretical study of structural, and electronic properties of NaZnAs compound is presented by performing ab initio calculations based on density-functional theory using the full-potential linear augmented plane wave (FP-LAPW). The generalized-gradient approximation (GGA) and the local density approximation LDA) are chosen for the exchange–correlation energy. The Engel-Vosko (EVGGA) formalism is applied for electronic properties The calculated structural parameters, such as the lattice constant, bulk modulus and pressure derivative, the electronic band structures and the related total density of states and charge density are presented. The high-pressure α phase of the NaZnAs is investigated and phase transition pressure from tetragonal to high-pressure phase is determined. We have found that the Nowotny–Juza compounds NaZnAs is direct gap semiconductor at ambient pressure. The bonding character and the phase stability of NaZnAs compound are discussed. The nature and the size of the band gap of NaZnAs compound are associated with the bonding character of two Kinds of bonds, namely, Na–As and Zn–As bonds.

Keywords: Electronic materials; Ab initio calculations; Electronic structure ;Phase transitions

1. Introduction

Generally the crystal structure of Nowotny–Juza compounds AIBIICV can be drived from the zinc-blende III-V compounds by transmuting the group III atom into an isovalent pair I+II, and are found to crystallize mostly in cubic zinc-blende-type related structures [1-6].NaZnAs form a special case ,wich is found to crystallize in tetragonal Cu2Sb-type of structure [1,7]. NaZnAs is also found to crystallize in the MgAgAs (order CaF2-) type structure [1, 8, 9].
Although Lithium Nowotny–Juza compounds are studied elsewhere, to the best of our knowledge there has missed investigation of NaZnAs compound in term of electronic, structural [1]. NaZnAs compound

which belong to the same group but with tetragonal Cu2Sb type structure (space group P4/nmm) [1] in contrast to cubic lithium semiconductor such as LiZnAS compound. In the present work, using the DFT approach we studied the tetrahedral Nowotny–Juza compound NaZnAs. We derived electronic properties for this compound and we also investigated the influence, of the pressure and As atomic on the electronic structure. In Section 2, we report some details about the. crystal structure and the numerical calculations We concentrate on the equilibrium lattice constant, bulk modulus in Section 3.1. We focus on the electronic properties in terms of band structures, density of states and charge density in Section 3.2 Finally; we draw conclusions in Section 4.

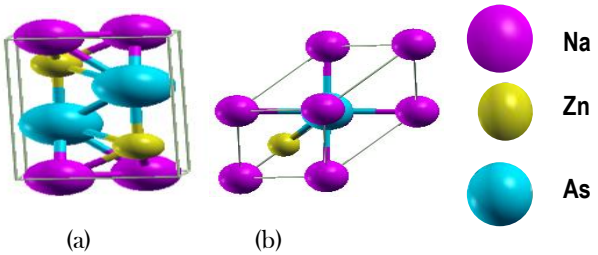
2. Calculation method

In this paper, we describe the results of the first principles electronic structure calculations of NaZnAs compound in the tetragonal Cu2Sb-type and cubic α (MgAgAs-type) of zinc blende-type, related structures .The calculation are performed using ab initio

calculations based on density-functional theory using the full-potential linear augmented plane wave (FP-LAPW).

2.1. Crystal structure

NaZnAs compound crystallize at ambient pressure in the tetragonal structure with space group (129) P4/nmm. The unit cell contains two molecules per formula unit this is shown in Fig. 1.In the cubic (α) phase under pressure, there are 3 atoms by unit cell is shown in Fig. 2. The calculations presented in this work were performed using the full potential linearized augmented plane wave (FP-LAPW) method. We augmented plane wave (FP-LAPW) method. We use the WIEN2K [10] implementation of the method which allows the inclusion of local orbitals in the basis improving upon linearization and making, possible a consistent treatment of the semicore and valence states in an energy window. The electron–electron interaction was treated within local density approximation (LDA) [11] and generalized gradient approximation (GGA) by Perdew, Burke and Ernzerhof PBE) exchange–correlation potential [12] In addition, and for the electronic properties we also applied the Engel-Vosko (EV-GGA) scheme [13].



(a) (b)

Fig..1. (a) Shematic diagram of the unit cell of NaZnAs in primitive tetragonal Cu_2Sb-type structure and (b) the unit cell of the α phase of cubic NaZnAs.

3. Results and discussion

3.1. Total energy calculations and phase transition

NaZnAs compound belong to Nowotny–Juza compounds AIBIICV which based on three main group elements (A, B and C). They can be viewed as zinc-blende III–V compound in which the III column has been disproportionated into AI + BII atoms [1,8,14].The most stable phase of NaZnAs in contrast to the most cubic Nowotny–Juza compounds which crystallize in α phase [1,8,14,15]. This fact is confirmed by Jaiganesh et al. [1] using the tight-binding linear muffin-tin orbital method within the local density approximation (LDA). The atomic position of NaZnAs in the tetragonal phase are Na (1/4, 1/4 , z) ; (3/4, 3/4, 1-z), Zn (1/4, 3/4, 0) ; (3/4 ,1/4, 0) , As (1/4, 1/4, z) ; (3/4, 3/4, 1-z),wich z parameter for NaZnAs compound is;Na (0.3596),And As is(0,7807).

this structure transforms to cubic α phase with Fm-3m space group and the atomic position of NaZnAs in the cubic α are Na (1/2, 1/2, 1/2), Zn (0, 0, 0), As (1/4, 1/4, 1/4). The structure of this compound were optimized by calculating the total energy as a function of volume, which was followed by fitting the results with Murnaghan equation of state [16].The calculated total energy versus volume using GGA approximation for NaZnAs compound in tetragonal and cubic α are shown in Table1

Phase	NaZnAs compound		
tetragonal	GGA This work	Exp [1,7,17]	Other work[1]
a(A°)	4.192	4.176	4.121
c(A°)	7.115	7.088	/
c/a	1.697	1.697	1.697
B (GPa)	49.54	/	111.95
B′	3.87	/	/
Emin (Ry)	-16878.8226	/	/
α-phase			
a(A°)	6.350	/	5.916
B (GPa)	39.93	/	107.11
B′	4.33	/	/
Emin (Ry)	--8439.3747	/	/

Table 1 Calculated lattice constants (a and c) in A, bulk modulus (B) in GPa and pressure derivative B′ at equilibrium volume using GGA compared to and other works of NaZnAs.

Table 1 presents our calculated values obtained after optimization compared with the available experimental data and other theoretical results [1,7,18]. It is clearly seen that for the compound, the GGA overestimate the lattice parameter, Generally speaking our lattice parameters are in good agreement with those found experimentally and theoretically reported in Refs. [1,7].

Hardness measures a material's ability to resist deformation. Bulk modulus is the best indicator of hardness for materials. To estimate the bulk modulus, A big discrepancy was found in the values of the bulk moduli between the calculated values and those of Jaiganesh et al. [1], which is probably due to fact that they used the TB-LMTO method [1] within the LDA approximation.

NaZnAs compound transform from the initial tetragonal structure to the cubic structure under pressure (fig 2). The stability of a particular structure is decided by the minima of the Gibbs energy given by [19]:

$$G = E_{tot} + PV - TS$$

Since the theoretical calculations are performed at 0K the free energy becomes equal to the enthalpy (H):

$$H = E_{tot} + PV$$

The transition pressure from tetragonal phase to the α-phase for NaZnAs compound are listed and compared with the previous calculations and experimental data [1] Table 2. We note that a big disagreement is observed between our results and those of Ref. [1].

This is due to the fact that they have predicted the existence of tetragonal phase over a long range very short range. However from our calculation we predict it over very short range about 1 GPa. This suggest that NaZnAs compound prefer to be in the α phase like the majority of Nowotny– Juza compounds this is shown in fig 2

		$Cu_2Sb \rightarrow$ α-phase	
		This work	other work[1]
NaZnAs	GGA	1.12	/
	LDA	1.26	15.75

Table.2.Calculated transition pressure values NaZnAs compound using LDA and GGA approximation

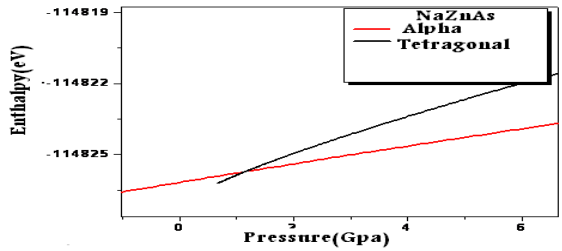


Fig.2. Variation of total enthalpy as a function of pressure of unit cell for tetragonal phase, α-phase using GGA for: NaZnAs compound

3.2. Electronic band structure and density of state

The self-consistent scalar relativistic band structures NaZnAs compound along representative symmetrical directions of the Brillouin zone were obtained in the tetragonal phase at equilibrium volume as well as at high pressure within the LDA, GGA and EV-GGA schemes. The Fermi level E_F is shown by a solide horizontal line. As a prototype we have shown the band structure and total density of states of NaZnAs using GGA approximation in the tetragonal and α- phase in Fig. 3. Accordingly, the conduction band minimum appears to be at the zone center C. Hence NaZnAs is direct gap semiconductor The calculated band gap $E_{\Gamma\Gamma}$ for NaZnAs is found to be 0.44 (0.39) eV using LDA (GGA), respectively in tetragonal phase The band structure calculated using the GGA and the EV-GGA for NaZnAs compound were similar except for the value of their band gap which was higher within the EVGGA. The band gap values are given in Table, 3 compared with available theoretical works.

compound	tetragonal	α-phase
NaZnAs		
LDA	0.44	0
GGA	0.39	0
EVGGA	0.79	0
Exp[1,7,17]	/	/
Other work[1,20]	0.163	0

Table.3 Band gaps of NaZnAs compound within LDA, GGA and EVGGA calculated in all phases tetragonal, and α phases (all values are in eV).

It is shown that the calculated energy gap values decrease with increasing (the size).

. However NaZnAs transforms to a metal under the effect of pressure

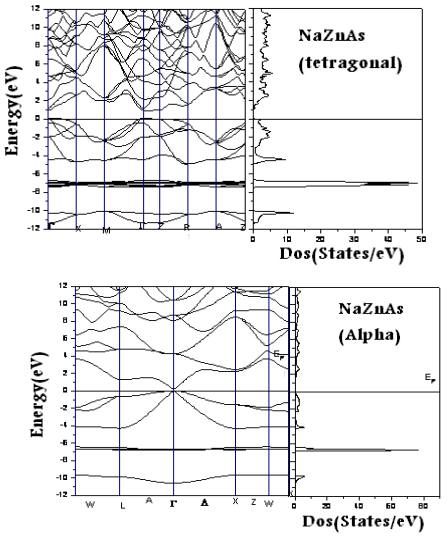


Fig 3. Band structure along the symmetry lines of the Brillouin zone and total densities of states for NaZnAs using EVGGA approximation for tetragonal phase. The position of the Fermi level is shown by the horizontal line for tetragonal phase and cubic α .

The total and partielle density of states (DOS) for NaZnAs compound at the equilibrium lattice constant is displayed at Fig.3. and Fig.4. respectively It is shown that there are two regions of the valence band, the upper valence bands are dominated by As-p and Zn-s, p orbitals while the bottom valence band is dominated by the As-s and Zn-d orbitals as shown in Fig. 4, the peaks are various according to the kind of structure.

The nature of the bond for NaZnAs compound. We have calculated the total charge density of NaZnAs compound, in different planes and for different Phases.

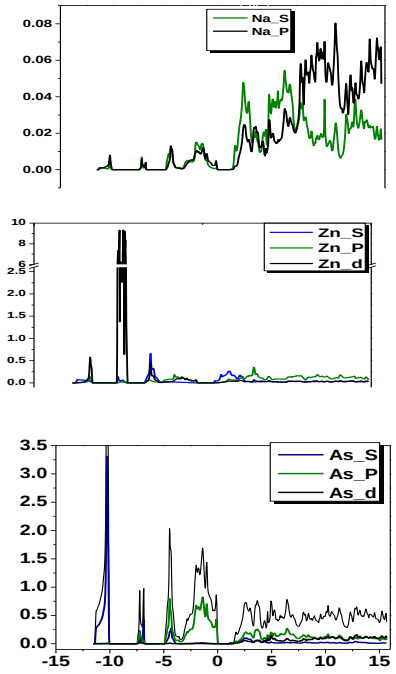


Fig 4. Partiell Density of states (Dos) for NaZnAs using EVGGA approximation for tetragonal phase.

Fig. 5 illustrates all the bonds in the (010) plane for tetragonal phase and (011) plane for α phase containing Na, Zn and As atoms. when the atom is As the Na–As bond becomes less ionic, and Zn–As becomes covalent in tetragonal phase.

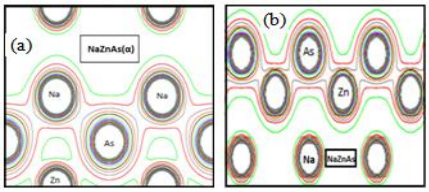


Fig .5.Calculated electron charge density in the (010) plane for tetragonal phase (b) and (011) plane for α-phase (b) of the NaZnAs compound.

4.Conclusions

The electronic and structural properties of NaZnAs, Nowotny–Juza compounds have been studied using both methods, the self consistent full-potential linear augmented plane wave (FP-LAPW). The bonding and the phase stability of NaZnAs compound is studied and it is concluded that the more stable phase. is the tetragonal phase under pressure this later transforms to α phase. The bulk modulus has been calculated using LAPW and gave excellent agreement with others. Basing on electronic band structure calculations NaZnAs is a direct band gap semiconductor in the tetragonal phase with band gap of 0.79 eV using EVGGA approximation The bonding in NaZnAs is characterized by the fact that Na–As and Zn–As bonds being nearly pure ionic and covalent, respectively in tetragonal phase . In α phase the small band gap It is predicted that under high pressure, NaZnAs is a metal.

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