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Research Article

Semiconducting Characteristic of Antiferromagnetic Al_4X_3Mn (X = P, As and Sb) Compounds with Ab Initio Simulation Methods

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ABSTRACT

This research reports the electronic characteristics of ternary aluminium-based Al_4X_3Mn (X=P, As and Sb) compounds for the most stable magnetic order which is A-type antiferromagnetic. The related systems are comforming 215 space number with P-43m space group which is simple cubic crystal structure. The computations in this research have been done within the framework of Density Functional Theory. The calculations utilized Perdew-Burke-Ernzerhof type correlation functionals within the meta-generalized gradient approximation. For considered four different type magnetic orders, the visualized volume-energy plots and the calculated formation energy values imply that the magnetic nature of these compositions is A-type antiferromagnetic. Besides, the investigated electronic natures in the detected stable magnetic phase of these systems are semiconductor since the band gaps were observed in their electronic band structures and density of states (E_g = 0.36 eV for Al_4P_3Mn, E_g = 0.33 eV for Al_4As_3Mn, and E_g = 0.18 eV for Al_4Sb_3Mn).

1. Introduction

The compounds which belong to Group III and V elements in periodic table, are highly preferred for electronic devices due to having some intriguing physical properties. High heat conduction, wide electronic bandgap and strong resistance to radiation are just some of the interesting features [1-6]. The materials containing the mentioned elements having wide application fields in the electronic device industry could be used in communication area and high-speed rail transportation [7-11]. In this regard, the material scientists have focused on the gallium- and aluminium-based compounds which are among these type materials, for a long time.

In a theoretical research, the thermal conductivity and some mechanical properties of GaAs, AlAs, and $Al_xGa_{1-x}As$ alloys were discussed [7]. In another study, the vibrational properties and dynamic stability of $Ti_xGa_nAs_m$ and $Ti_xGa_nP_m$ compounds were studied by using ab initio calculations within GGA and LDA approximations [12]. Also, the half-metallic nature of $Ti_xGa_{1-x}P$ was presented by some other researchers [13-15] .

Furthermore, recently, the magnetic nature and electronic characteristic of Ga_4P_3Mn and Ga_4As_3Mn compounds were investigated with ab initio simulation methods [16]. In particular, the obtained observations and results in the mentioned studies in references [7, 12-16] formed the main motivation of this study.

For decades, material scientists have investigated many physical properties such as electronic behavior, magnetic nature, thermodynamic or thermoelastic properties, of solid crystalline materials theoretically, by using ab-initio simulation approaches grounded density functional theory (DFT). These type of

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computations are very useful to understand material and encourage related experimental and theoretical studies [17-22].

In this regard, for this research, ab-initio simulation methods have been employed by using appropriately normed and strongly constrained semilocal density functional, (METAGGA-SCAN) meta-generalized gradient approximation. Also, it has been found that ternary aluminum-based Al_4X_3Mn (X=P, As, and Sb) systems have A-Type antiferromagnetic nature and semiconducting characteristic. Despite having a small band gap, these types of materials may find applications in optoelectronics [23]. Therefore, these new ternary aluminium-based materials, due to having well physical properties such as semiconducting behavior could have large usage in some technological and industrial applications.

2. The Computational Details

The structural and electronic characteristics of Al_4X_3Mn (X: P, As, Sb) compounds have been investigated applying Vienna Ab-initio Simulation Package (VASP) [24, 25] with projector augmented wave (PAW) approach [26] based on Density Functional Theory (DFT) [27, 28]. The Kohn-Sham equations have been solved constantly until every pressures and forces on each atom reached zero.

The calculations utilized PBE (Perdew-Burke-Ernzerhof) type correlation functionals and employed structure was META-GGA (Meta Generalized Gradient Approximations) [29]. In order to express interactions among electrons and ion cores, PAW (projector-augmented) method has been considered. The valence electron configurations for Aluminum (Al) and Manganese (Mn) atoms are given $3s^2\ 3p^1$ and $4s^2\ 3d^5$. Also, for the Phosphorus (P), Arsenic (As) and Antimony (Sb) atoms are $3s^2\ 3p^3$, $4s^2\ 3d^{10}\ 4p^3$ and finally $5s^2\ 4d^{10}\ 5p^3$ with respectively.

To ensure accuracy, a 12×12×12 Monkhorst and Pack (MP) scheme k-point mesh has been employed [30]. The Methfessel–Paxton smearing method with a 0.01 eV smearing parameter has been adopted and the iterations have been continued as far as all the forces on each ion become lower than 10^{-8} eV/Å. Further, the convergence criteria for the iteration steps has been set at 10^{-9} eV. The cut-off energy has been set at 900 eV. In addition, the three dimensional visualization an X-ray diffraction pattern have been achieved by using VESTA [31].

With the aim of picking most convenient magnetic phase 2x2x2 super-cells have been created and ground state energies have been determined. And finally structural parameters, electronic band structures and density of states have been inspected in most suitable magnetic order. Furthermore, for the electronic part, 6×6×6 MP (Monkhorst-Pack) k-point mesh has been used for sampling reciprocal space. Also, for the calculation IBRION = -1, EDIFF = 1.E-9, EDIFFG = -1.E-8 and finally cut-off energy has been chosen as 600 eV

3. Results

3.1. Structural properties

Ternary aluminum-based a of Al_4X_3Mn compounds, where X represents P, As or Sb atoms, possess a simple cubic structure with 215 space number with $P\bar{4}3m$ space group. The 3d (three-dimensional) primitive cell of Al_4X_3Mn (X: P, As, Sb) materials consists of 8 atoms have been given in Figure 1 with X-ray diffraction pattern (XRD). Also, it has been revealed that the 2θ values of the maximum peak is 27.64 degrees for Al_4P_3Mn, 26.81 degree for Al_4As_3Mn and finally 25.07 degree for Al_4Sb_3Mn in figure 1. As can be clearly seen from the figure, it has been observed that the maximum peak value decreased as the atomic radius increased.

In this research concerning to determine most convenient magnetic phase, three types of antiferromagnetic orders as A-type, C-type, and G-type and ferromagnetic phases has been considered [32]. Figure 2 presents the total energies-volume plots for these magnetic phases which have been plotted by using Vinet equation [33]. The results suggest that the A-type antiferromagnetic order is the most appropriate for all three materials, as the ground state energies have been very closely grouped.

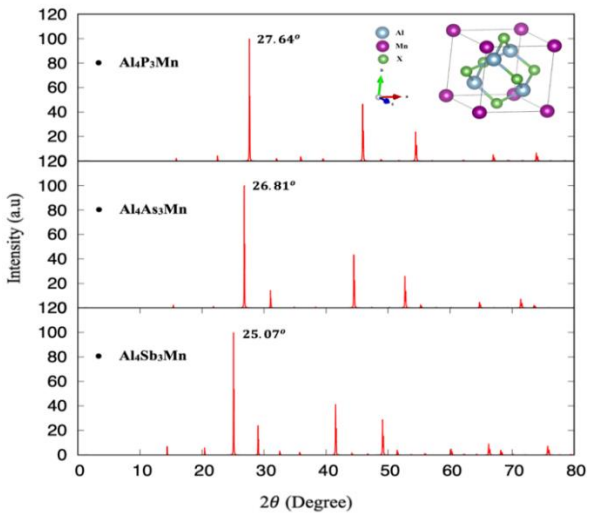

Figure 1. The three-dimensional (3d) crystallographic arrangement and X-Ray diffraction pattern (XRD) of Al_4X_3Mn (X: P, As, Sb). Where abbreviation of arbitrary unit is a.u.

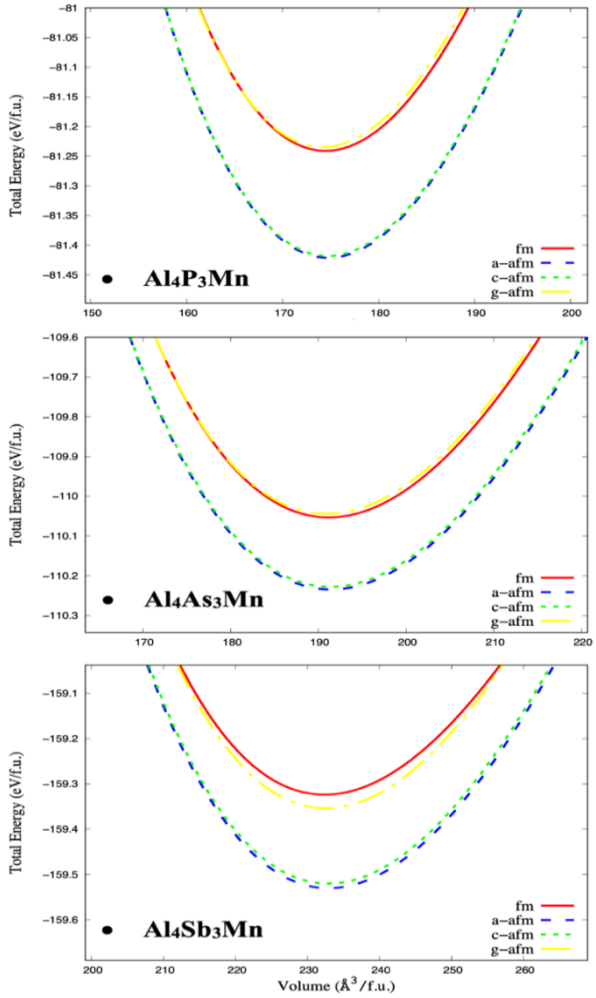

Figure 2. The total energy-volume plots for three types of A, C and G type antiferromagnetic order and for the ferromagnetic order; a) Al_4X_3Mn (X: P, As, Sb).

Table 1. The determined bond lengths (d), lattice parameters (a), and the formation enthalpies (ΔE_f) for the Al_4X_3Mn (X: P, As, Sb) compounds.

Compounds	a (Å)	$d_{Al\text{-}X}$ (Å)	$d_{Al\text{-}Mn}$ (Å)	ΔE_f (eV/f.u.)
Al_4P_3Mn	5.58601	2.38621	2.52264	-2.5387500 -2.5384375 -2.5443750 -2.5446875
Al_4As_3Mn	5.75533	2.47240	2.55336	-3.4393750 -3.4390625 -3.4443750 -3.4446875
Al_4Sb_3Mn	6.14708	2.67203	2.63142	-4.9787500 -4.9796875 -4.9850000 -4.9856250

In the Equation 1, $E_{Al_3X_3Mn}$ represents the total energies where X denotes P, As or Sb elements. Also, the other terms represent ground state energies of each elements. Table 1 provides information on the bond lengths (d) and lattice parameters (a), showing that both quantities increased with the radius of X atoms as expected. Notably, the determined formation energies of all three compounds are negative for all magnetic orders. It indicates that, their energetic feasibility and stability for structural synthesis. In addition the most suitable magnetic arrangements for all three materials are the A-type antiferromagnetic order, as it exhibits lowest formation energies. These findings align with the trends observed in the volume-energy plots in Figure 2. Therefore, our materials structurally stable and thermodynamically synthesizable.

$$\Delta E_f = E_{Al_4X_3Mn} - \left(4E_{Al}^{bulk} + 3E_X^{bulk} + E_{Mn}^{bulk}\right) \quad (1)$$

3.2.The observations about the electronic characteristics

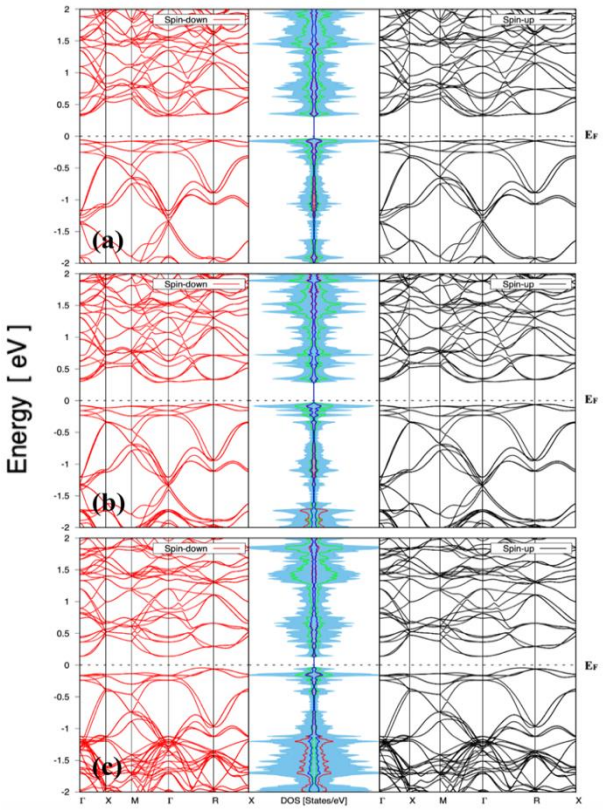

Figure 3. The determined electronic band structures for spin majority orientation (right) and spin minority orientation (left) with Density of States for (a) Al_4P_3Mn (b) Al_4As_3Mn and (c) Al_4Sb_3Mn. Also, the Fermi energy level (E_F) is set to zero and it is represented with the black dashed line.

The electronic features of the materials have been analyzed using the calculated partial and total density of states with the electronic band structures, depicted in Figure 3. The electronic band structures for three compounds have been visualized onward the high symmetry points and META-GGA has been applied to both spin majority and spin minority states. The results show that all three ternary aluminium-based materials in this study, exhibit semiconductor behavior, with an indirect band gap (R to Γ point) of E_g = 0.36 eV for Al_4P_3Mn, E_g = 0.33 eV for Al_4As_3Mn, and E_g = 0.18 eV for Al_4Sb_3Mn. Additionally, these band gaps are inversely proportional to the atomic radius of P, As, and Sb atoms, which are 98, 114, and 133 pm, respectively.

Also, Figure 4, illustrates the partial (PDOS) and total (TDOS) orbital projected density of states for each atom in the Al_4X_3Mn (X: P, As, Sb) compounds. For all three crystal systems, transition metal Manganese (Mn) atom contribute significantly to the total density of states, particularly for the energy range from -0.5 eV up to Fermi energy level. The dominant orbital in this range are 3d states of Mn atoms. One notable difference between the materials, is that hybridizations of Antimony (Sb) atoms p-orbitals around Fermi energy levels. Therefore, the band gap (E_g = 0.18 eV) for the Al_4Sb_3Mn compound is smaller than the others.

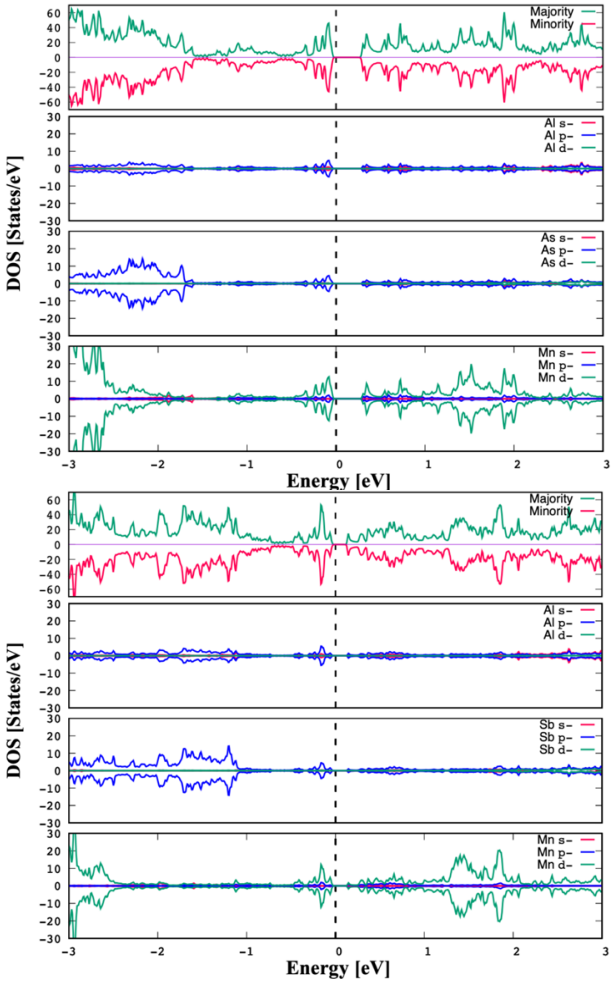

Figure 4. The orbital projected Density of states (DOS) for the elements in Al_4X_3Mn (X: P, As, Sb) compounds for both spin up and down case respectively.

4. Conclusion

For this computational research, the structural and electronic features of Al_4X_3Mn (X: P, As, Sb) compounds have been examined in detail. These compounds, denoted as simple cubic structure in accordance having a space number of 215 and its space group is $P\bar{4}3m$. Despite of the ground state energies for all three compounds are

quite close, it becomes evident that the firmly the most suitable magnetic phases are the A-type antiferromagnetic order for all three materials. The almost same behavior observed in the spin majority and spin minority states of the plotted electronic band structures also shows antiferromagnetic tendency.

Moreover, the determined formation energies of all three compounds are negative for all considered magnetic orders. It indicates that, the materials energetically feasible and stable for structural synthesis. The partial and total density of states and the electronic band structures reveal that our materials exhibit semiconductor behavior with an indirect band gap of 0.36 eV for Al_4P_3Mn, 0.33 eV for Al_4As_3Mn, and finally 0.18 eV for Al_4Sb_3Mn compounds. The observed their semiconducting characters and the calculated negative formation energies may suggest that the mentioned materials are good candidates for use in particularly semiconductor device technology.

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This study does not require ethics committee permission or any special permission.

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The authors of the paper declare that they comply with the scientific, ethical and quotation rules of SAUJS in all processes of the paper and that they do not make any falsification on the data collected. In addition, they declare that Sakarya University Journal of Science and its editorial board have no responsibility for any ethical violations that may be encountered, and that this study has not been evaluated in any academic publication environment other than Sakarya University Journal of Science.

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