# Investigation of Al$_3$Ti$_{0.5}$V$_{0.5}$ Alloy

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The FP-LAPW method is employed and the gradient generalized approximation (GGA) is used to treat the exchange-correlation potential. In this study we considered the Al$_3$Ti$_{0.5}$V$_{0.5}$ alloy case. In which we investigated the structural stability of the tetragonal D0$_{22}$ and cubic L1$_2$ ternary alloy Al$_3$Ti$_{0.5}$V$_{0.5}$ relative to the Al$_3$Ti and Al$_3$V. The total energy calculation as a function of its volume shows that the tetragonal phase is the more stable one. The formation enthalpies are calculated. The total and partial density of states exhibits a deep-pseudo gap near the Fermi level and the transition metal contribution to the DOS is almost entirely formed by the *d*-electrons.

## 1. Introduction

Transition metal based trialuminides Al$_3$M exhibits a unique combination of properties such as high melting points, low mass densities and oxidation resistances. A great deal of research has been devoted to investigating these materials for the understanding of their electronic properties and structural phase stability [1-3]. Among these Al$_3$M alloys (where M is the transition Ti, V, Zr, Nb, Hf…), the possible crystal structures are D0$_{19}$, D0$_{22}$, D0$_{23}$ and L1$_2$ [4]. Al$_3$Ti in particular has a very low density (3.3g/cm$^3$), yet it is very brittle. In the past years, many attempts were undertaken in order to correlate the mechanical properties of TM aluminides with their crystal structure in a wide scheme with the electronic structure [5-8]. The

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related cubic $L1_2$ structure is formed from $D0_{22}$ which provides more slip systems and enhances ductility, by the addition of ternary elements, such as Cr, Mn, Fe, Co, Ni, Cu, V and Zn [9,10].

## 2. Computational details

We used the full-potential linearized augmented plane wave (FP-LAPW) method in order to calculate the structural and electronic properties of $Al_3Ti_{0.5}V_{0.5}$ alloy, using Vienna package wien2k [11]. Exchange and correlation effect are treated by the gradient generalized approximation (GGA)[12]. Basis functions were expanded in combinations of spherical harmonic functions inside non-overlapping spheres surrounding the atomic sites (Muffin-Tin(MT) spheres) and in Fourier series in the interstitial region. In the MT spheres the l-expansion of the non-spherical potential and charge density was carried out up to $l_{max} = 10$. The wave functions in the interstitial region were expanded in plane waves with $R_{mt}* k_{max} = 8$ (where $R_{mt}$ is the average radius of the MT spheres and $k_{max}$ is the cutoff). The self-consistent calculations are considered to be converged only when the calculated total energy of the crystal converged to less than 1 mRyd. In the $D0_{22}$, we have adopted the radii values of 2.0 a.u for aluminum and 2.3 a.u for titanium and vanadium, in $L1_2$ the values are 2.2 a.u and 2.6 a.u for aluminum and transition metals respectively. The numbers of special k-points used in the irreducible Brillouin zone for $D0_{22}$ ($L1_2$) are 59 (56).

## 3. Results and discussion

In this study, we have calculated the total energy of the ternary alloy ($Al_3Ti_{0.5}V_{0.5}$) formed by substitute the Ti (0.5, 0.5, 0.5) in $D0_{22}$ elementary cell by Vanadium atom. Show the space group change from I4/mmm (n° 139) to P4/mmm (n° 123), in addition to Wyckoff position Ti (1a) and V (1d) sites there are three aluminium sites, $Al_1$ (1b)(0.0, 0.0, 0.5), $Al_2$ (1c)(0.5, 0.5, 0.0), and $Al_3$ (4i)(0.5, 0.0, 0.25). For $L1_2$, we have used supercell of ($1\times1\times2$) primitive cells for $L1_2$. The Vanadium atom occupied the (0, 0, 0.5) site (Wyckoff 1b). However the number of the symmetry operation is reduced to 16 operations (space group n° 123) in lieu of 48 operations for $L1_2$

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structures. For Aluminium positions there three sites $Al_1$ (1d), $Al_2$ (1c) and $Al_3$ (4b). We cannot compare our results with others results, because are not available. Therefore our calculations are a prediction and can be used as a reference for future studies.

### 3.1. Total energy

We have investigate the structural stability of the hypothetical tetragonal and cubic ternary alloys $Al_3(Ti_{0.5}V_{0.5})$ relative to the $Al_3Ti$ and $Al_3V$. The total energy calculation of $Al_3(Ti_{0.5}V_{0.5})$ as a function of its volume show that the tetragonal phase is the more stable one. The total energy difference between these phases is around 82 meV/atom. The lattice constants the bulk modulus and its derivative are reported in table 1. For $D0_{22}$ phase: the equilibrium lattice parameters are a=3.809Å and c=8.470Å, while the average value of lattice constants for $Al_3Ti$ and $Al_3V$ are a=3.806 Å and c=8.478 Å. This verified the Vegard's law with 0.012 for the Bowing factor. The bulk modulus is equal to 112 GPa, the average value of the corresponding parameter for both binary compounds is 111.5 GPa. For $L1_2$ phase: the Bowing factor is equal to 0.02 and the bulk modulus is 110 GPa. The figure 1 shows the variation of formation enthalpy for $Al_3(Ti_xV_{1-x})$ (x=0, 0.5, 1) in both phases, on observe that the variation is nearly linear.
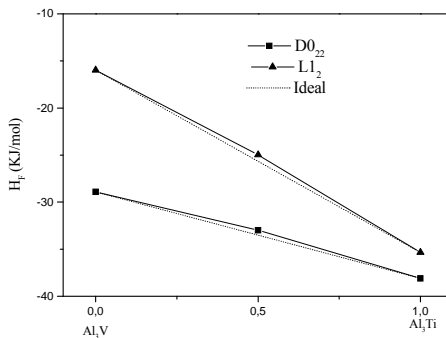


Fig. 1: calculated formation enthalpy of $Al_3(Ti_{0.5}V_{0.5})$ in D022 and L12 phases. The reference states are fcc-Al, bcc-V and hcp-Ti

## 3.2. The density of states

The electronic structures of trialuminides compounds are treated with many theoretical methods, and all agree unanimously on the existence of the pseudo-gap [13-16]. The density of states (DOS) for $Al_3(Ti_{0.5}V_{0.5})$ exhibits also an pseudo-gap near the Fermi level. In the $L1_2$ case, the Fermi level is on the right side of the minimum (pseudo-gap) of the density of states. While in the $D0_{22}$ case, the Fermi level is on the left side. The *Ti* and *V* atoms contribution to the DOS is almost entirely formed by the *d*-electrons. This pseudo gap is due to the strong hybridisation between the *d* states of transition metal and the Al (*s, p*) states. In table1 we report the values of total density of states at Fermi level $N(E_F)$, and the DOS at minimum $N(E_{min})$ and corresponding energy $E_{min}$ for D022 and L12 structures, respectively.



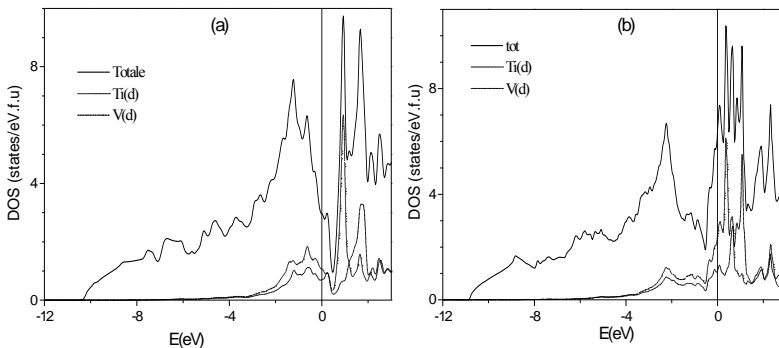Fig. 2: The DOS of $Al_3(Ti_{0.5}V_{0.5})$ in $D0_{22}$ (a)and $L1_2$ (b) structures. The dashed and dots lines presents the Ti(*d*) and V(*d*) contribution respectively

Table 1: constants $a$ (Å)and $c$(Å), $c/a$ ratio, bulk modulus B(GPa) and their derivative B'. the formation enthalpy (KJ/mol). the total density of states at Fermi level $N(E_F)$( states/eV-atom), and the DOS at minimum $N(E_{min})$(states/eV-atom) and corresponding energy $E_{min}$ (eV). For $D0_{22}$ and $L1_2$ structures.

| | $Al_3Ti$ | $Al_3Ti_{0.5}V_{0.5}$ | $Al_3V$ |
|---|---|---|---|
| $D0_{22}$ | | | |
| $a$ | 3.844 | 3.809 | 3.768 |
| $c$ | 8.623 | 8.470 | 8.313 |
| c/a | 2.242 | 2.223 | 2.206 |
| B | 104 | 112 | 119 |
| B' | 3.93 | 3.76 | 3.77 |
| ΔH | - | -32.99 | -28.91 |
| $N(E_F)$ | 38.11 | 0.370 | 0.217 |
| $E_{min}$ | 0.445 | 0.477 | 0.12 |
| $N(E_{min})$ | 0.862 | 0.121 | 0.07 |
| | 0.105 | | |
| L12 | | | |
| A | | 3.941 | 3.905 |
| B | 3.978 | 110.2 | 116 |
| B' | 102 | 4.23 | 3.71 |
| ΔH | 3.93 | -24.97 | -15.97 |
| $N(E_F)$ | - | 0.800 | 0.840 |
| $E_{min}$ | 35.35 | -0.545 | -0.689 |
| $N(E_{min})$ | 0.632 | 0.239 | 0.241 |
| | - | | |
| | 0.394 | | |
| | 0.217 | | |

## 4. Conclusion

As it is known the trialuminides $Al_3Ti$ and $Al_3V$ crystallize in the $D0_{22}$, the $L1_2$ phase is the metastable one. We have investigated the structural and phase stability of the ternary $Al_3Ti_{0.5}V_{0.5}$ . We found that the $D0_{22}$ is the more stable phase. The total energy difference between these phases is around -82 meV/atom. The formation enthalpies are -32.99 and -24.97 KJ/mol for $D0_{22}$ and $L1_2$. The

pseudo-gap is present in density of states. In the $D0_{22}$ case, the values of the DOS at the Fermi level are 0.37 stetes/eV-atom low than that for $Al_3Ti$. Therefore, the ternary alloy is the more stable one in the rigid band sense. In general, the ternary alloy posse's intermediary properties electronic and mechanic relatively to the binary compounds.

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