An *ab initio* Study of Cr and Mn Doped MAX Phase TiMSiB

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***Abstract*—MAX phases, which are widely studied experimentally and theoretically, have general formula of $M_{(n+1)}AX_n$, where M is transition metals, A is A group element and X is C and N. In this study, the structural, mechanical and electronic properties have been researched for hypothetical MAX phase TiMSiB, where M is Cr and Mn by applying ab initio calculations. Initially, structural optimizations have been completed and the outcomes crosschecked with the studies of Ti_2SiB in literatures [1]. After optimization process have been achieved, the mechanical stability has been proved. Moreover, Young, Bulk, Shear modules and Poisson ratio for the compounds have been estimated by using elastic constants. Also, to understand the anisotropic behavior of the materials, directional dependent two and three-dimensional mechanical properties have been plotted. Finally, electronic band structures and corresponding density of state (DOS) have been plotted.**

Keywords—Hypothetical MAX phase, ab initio calculations, structural, mechanical and electronic properties.

I. Introduction

MAX phases, have general formula of $M_{(n+1)}AX_n$, where M is transition metals, A is A group element and X is C and N. This type of materials has been studied widely both experimental and theoretical applications [1-5]. Also, MAX phases have been used in engineering; lithium ion batteries, durable coatings, superconducting materials, spintronic devices and the nuclear industry [6, 7].

However, common studies have been done until recent years, to leave X atoms as C or N and focused on M transition metals, in some studies X atoms replaced with B [1, 8, 9]. For this purpose, we have doped Cr and Mn to M site atoms and replace X atoms with B. Also, the compounds include B, usually have interesting mechanical, physical properties and have wide range of technological applications.

In this study, the structural, mechanical and electronic properties of the compound TiMSiB (M: Cr and Mn) have been computed by using VASP. In which, Young, Bulk, Shear modules and Poisson ratio for the compounds have been estimated by using elastic constants. Also, to understand electronic behavior, the electronic band structure and corresponding partial and total density of state graphs for the first Brillouin zone along high symmetry directions plotted.

II. Computational Details

All the *ab initio* calculations have been done with VASP (Vienna ab Simulation Package) [10] by using GGA (Generalized Gradient Approximation). Also, for the atoms in material PBE (Perdew, Burke and Ernzerhof) type pseudo-potential have been used [11]. In addition, for the calculations 16x16x4 Monkhorst-Pack k-point mesh and 500 eV cut-off kinetic energy has been chosen [12]. Elastic constants measured by stress strain method. Finally, for the atoms Ti, Cr, Mn, Si, B valance electron configurations are; $4s^2\ 3d^2$, $4s^1\ 3d^5$, $4s^2\ 3d^5$, $3s^2\ 3p^2$, $2s^2\ 2p^1$ respectively.

III. Results and Discussion

The phase of TiMSiB crystallize in a hexagonal structure with the space group $P6_3/mmc$, in which the Ti and M occupies at 4f (1/3, 2/3, z), Si at 2d (1/3, 2/3, 3/4), and B at 2a (0,0, 0) Wyckoff positions.

As seen in Fig. 1, its three-dimensional crystal representation is given. Also, in Fig. 2 X-ray diffraction pattern shows that our materials have polycrystal behavior. Its maximum pick is around 40.9 degree.

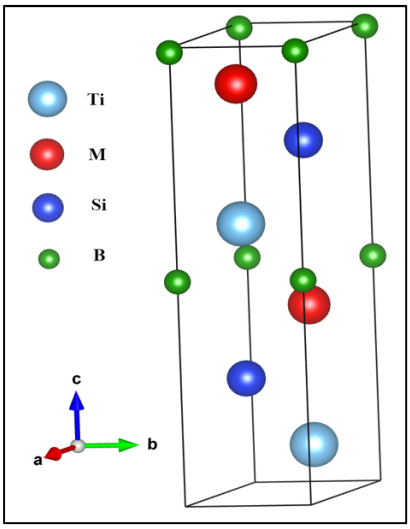

Fig. 1. Three-dimensional crystal representation of TiMSiB (where M is Cr and Mn).

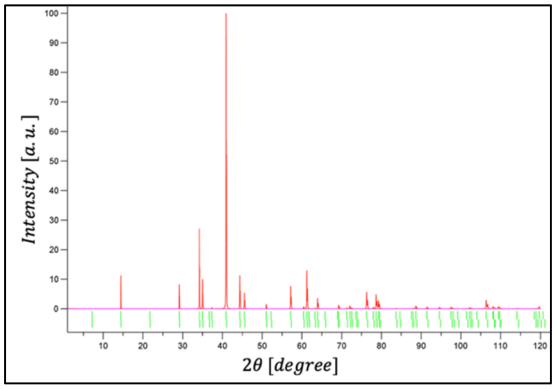

Fig. 2. X-Ray diffraction pattern of representation of TiMSiB where a.u. is arbitrary unit.

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A. Mechanical Properties

For thermodynamic stability formation enthalpy of the materials must be negative. Formation enthalpy have been calculated from the formula: $\Delta H_f = E_{TiMSiB} - (E_{Ti} + E_M + E_{Si} + E_B)$, and tabulated at Table 1. All the independent elastic constants (C_{ij}) have been calculated from stress-strain method and listed at Table 2.

Table 1. Lattice parameters (a, c) and formation enthalpies (ΔH_f) for TiCrSiB and TiMnSiB.

Compounds	a=b(Å)	c(Å)	ΔH_f (eV / f.u.)
TiCrSiB	3.0249	12.2465	-2.59
TiMnSiB	3.0043	12.0936	-2.15

Table 2. Elastic constants (C_{ij}) for Cr: TiCrSiB and Mn: TiMnSiB.

Mat.	C_{11} (GPa)	C_{12} (GPa)	C_{13} (GPa)	C_{33} (GPa)	C_{44} (GPa)	C_{44} (GPa)
Cr	224.7	125.4	143.7	274.3	141.1	49.6
Mn	241.3	122.7	140.0	292.3	174.3	59.3

Bulk (B), Shear (G) and Young's (E) module, anisotropy parameters ($A_{1,2}$ and A_3) and finally hardness of the material (H_V) have been estimated by using elastic constants for hexagonal crystal structures and tabulated in Table 3 and Table 4.

Table 3. Bulk (B), Shear (G) and Young's (E) module and Poisson Ratio (ν) for TiCrSiB and TiMnSiB.

Compounds	B (GPa)	G (GPa)	E (GPa)	ν	B/G
TiCrSiB	170.5	77.6	202.1	0.302	2.197
TiMnSiB	174.2	94.2	239.4	0.271	1.849

Table 4. Anisotropy parameters ($A_{1,2}$ and A_3) and hardness of the material (H_V) for TiCrSiB and TiMnSiB.

Compounds	$A_{1,2}$	A_3	H_V (GPa)
TiCrSiB	2.67	1	9.29
TiMnSiB	2.75	1	14.1

It is clearly seen from the Table 3, B/G ratios is higher than the critical value 1.75, so that means the materials is ductile [13]. If the Poisson Ratio (ν) is around 0.1 materials have covalent bonding, if around 0.25 they have ionic bonding. Therefore, in our case, TiMnSiB compound has ionic bonding. Also, material is called hard if stiffness (H_V) value is between 10-20 GPa [14]. TiMnSiB compound considered as hard material. Another important parameter for engineering is the anisotropy parameter. It shows the behavior of the material under compression and shearing. If these values are close to 1, it shows that there is an isotropy in the material. Our materials are isotropic in A_3 and anisotropic for the other directions. To understand that anisotropic behavior better, we have plotted the two and three-dimensional directional dependent Young Module, Linear Compressibility, Shear Modules and Poisson Ratios in Fig. 3.

B. Electronic Properties

The electronic band structure for the first Brillouin zone along high symmetry directions plotted and at Fig. 4 for (a) TiCrSiB and (b) TiMnSiB. It is seen that there isn't band gap over Fermi Energy Level. Therefore, our materials show metallic behavior. Also, orbital projected total and partial density of states given at Fig. 5. It appears that almost all the contributions come from 3d orbital of Ti atom and transition metals (Cr and Mn).

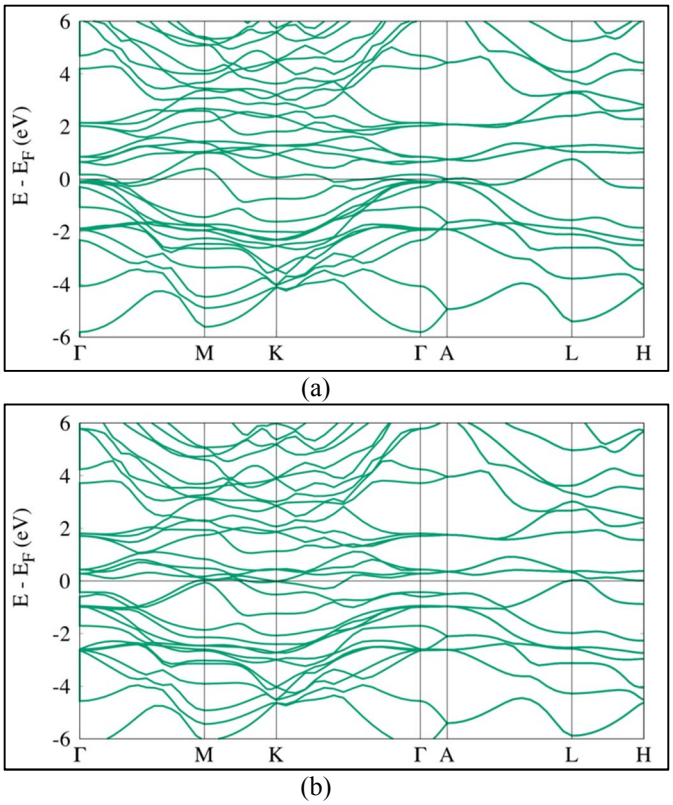

Fig. 4. Electronic band structure of (a) TiCrSiB and (b) TiMnSiB.

I. CONCLUSION

The structural, mechanical and electronic properties of the compounds TiMSiB (M: Cr and Mn) have been computed by using VASP. The material thermodynamically, mechanically stable and could be synthesized. Mechanically the material is ductile and counted as hard. Also, electronic band structure and density of states graphs illustrate that the compounds have metallic nature.

This study proves that, Cr and Mn doped materials compatible with the hypothetical MAX phase materials in literature. Also, as in MAX phases, materials could be used various technological applications such as; lithium ion batteries, durable coatings, superconducting materials, spintronic devices and the nuclear industry.

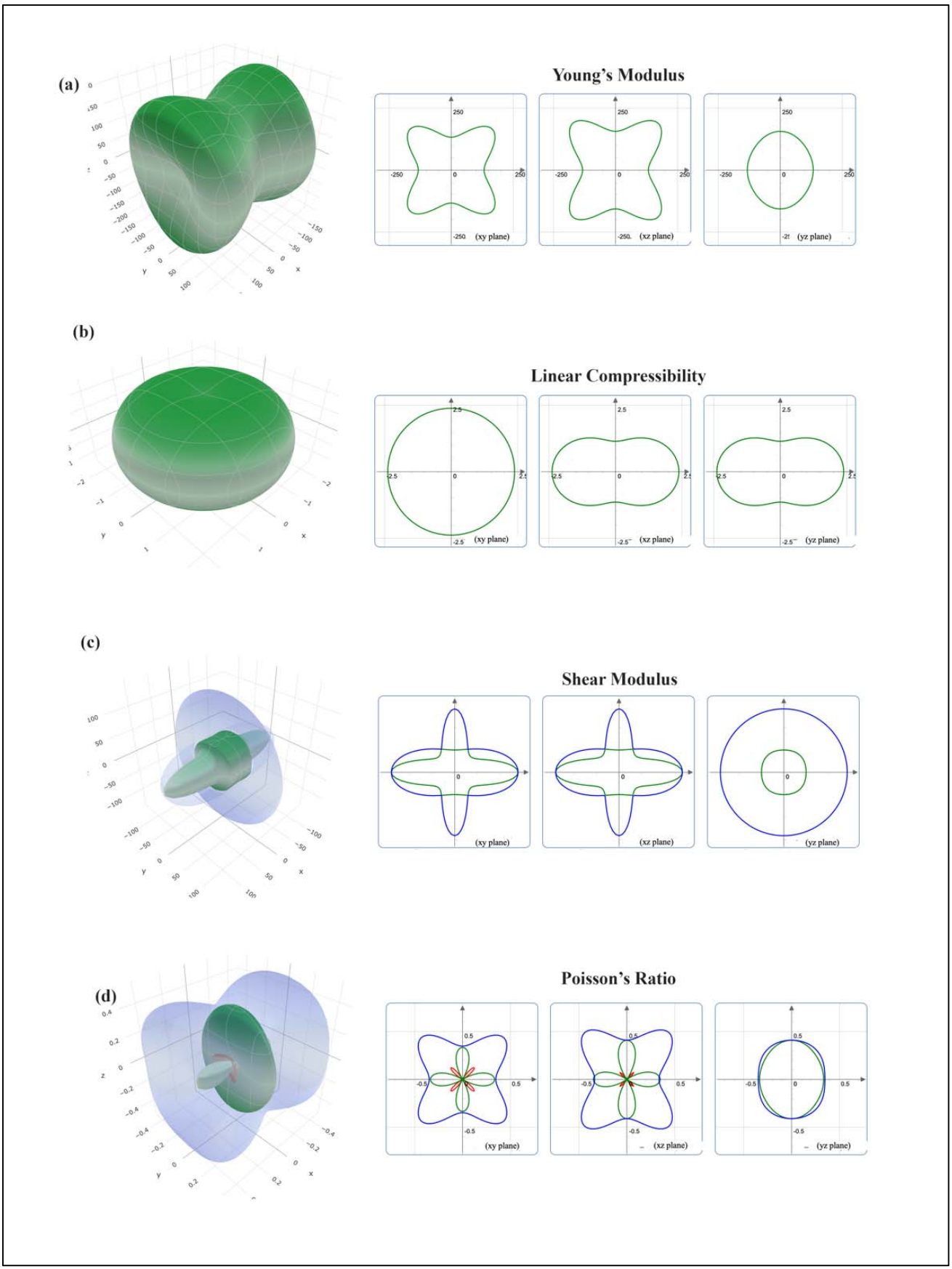

Fig. 3. Two and three-dimensional directional dependent Young Module, Linear Compressibility, Shear Modules and Poisson Ratios of TiMSiB.

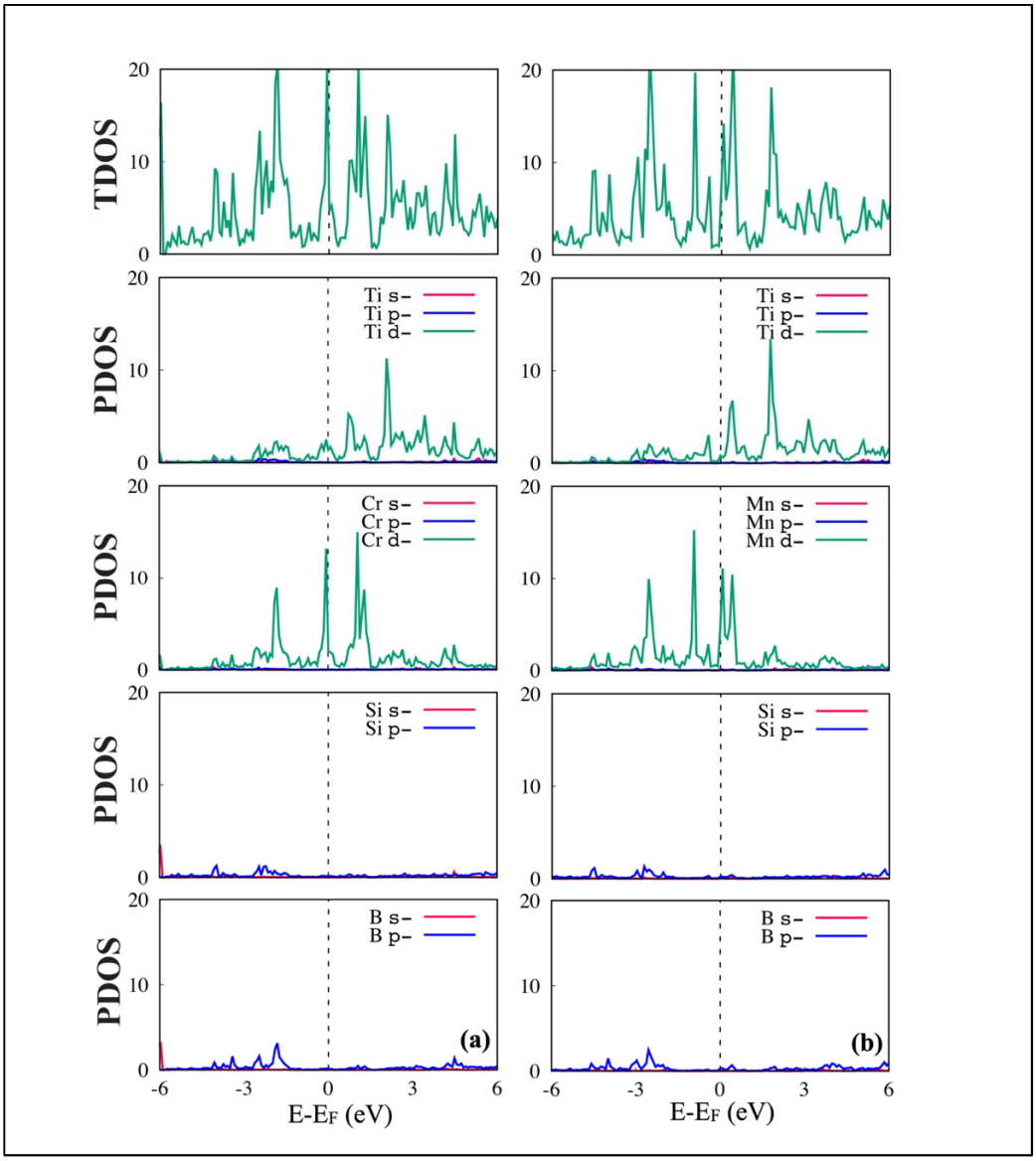

Fig. 5. Orbital projected total and partial density of states (a) TiCrSiB and (b) TiMnSiB.

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