

**COMPUTATIONAL MODELLING OF TiPt and TiPtCo-M (M=Ta,
V, Hf) SHAPE MEMORY ALLOYS**

by

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Abstract

First-principles density functional theory has been used to study the stabilities of binary TiPt, TiTa, TiNi and TiCo potential shape memory alloys. Furthermore, ternary alloys $\text{Ti}_{50}\text{Pt}_{50-x}\text{M}_x$ with V, Ta, Hf and quaternary $\text{Ti}_{50}(\text{PtCo})_{50-x}\text{Ta}_x$ systems were also investigated. The structural, electronic and mechanical properties were deduced to mimic the stabilities of these alloys. Furthermore, their vibrational stability, x-ray diffraction and temperature dependence have been examined.

The structures were subjected to full geometry optimization to obtain equilibrium lattice constants. It was found that the equilibrium lattice parameters for all the binary systems are in good agreement with experimental results to within 5%. The heats of formation (ΔH_f) were calculated to determine the thermodynamic stability of the B2 TiM systems. It was revealed that TiPt is the most energetically favourable (most stable) whereas TiTa is the least favourable due to high ΔH_f value (less stable). In addition, electronic properties suggest that TiPt, TiNi and TiCo systems are stable with TiTa being the least favourable consistent with the ΔH_f . The elastic properties were also calculated to mimic the mechanical stability of these alloys. TiNi, TiCo and TiTa were found to be mechanical stable whereas TiPt is unstable. This behaviour is consistent with the phonon dispersion curves for TiPt and TiCo. TiCo structure, in particular is the most stable in line with the predicted phonon dispersion.

The effect of alloying on $\text{Ti}_{50}\text{Pt}_{50-x}\text{M}_x$ ($M = \text{V, Ta, Hf}$) ternary system was carried out using the supercell approach. It was observed that the lattice parameters decrease minimally with an increase in V and increases with an increase in Ta and Hf content. The structures

become thermodynamically less stable with an increase in V, Ta and Hf content, as depicted by heats of formation. The shear modulus (C') of $Ti_{50}Pt_{50-x}M_x$ increases with an increase in M (V, Ta and Hf) concentration suggesting mechanical stability of these alloys. This has been confirmed from the phonon curves where the phonon soft modes are reduced and tend to disappear with increasing content of the alloying elements. Thus the results suggest that the V, Ta and Hf addition reduces the transformation temperatures of the TiPt alloy as indicated by its higher shear modulus C' .

Furthermore, it was observed that the lattice parameters of the quaternary system decrease with an increase in Ta content in the system. Thus ΔH_f of the B2 and B19 $Ti_{50}Pt_{43.75-x}Co_{6.25}Ta_x$ and B19 $Ti_{50}Pt_{31.25-x}Co_{18.75}Ta_x$ alloy system showed that the 6.25 at.% Ta addition is energetically most favourable ($\Delta H_f < 0$). The DOS behaviour confirms that the 6.25 at.% Ta is least favourable whereas for B19, the 6.25 at.% Ta is most favourable. The elastic constants for B19 and B2 show the positive shear modulus (mechanical stability). Moreover, the phonon dispersions and phonon density of states for the B2 and B19 $Ti_{50}Pt_{43.75-x}Co_{6.25}Ta_x$ and $Ti_{50}Pt_{31.25-x}Co_{18.75}Ta_x$ were calculated and are consistent with the elastic constant.

The LAMMPS code was employed to investigate the temperature dependence of the B19 $Ti_{50}Pt_{43.75-x}Co_{6.25}Ta_x$ and $Ti_{50}Pt_{31.25-x}Co_{18.75}Ta_x$ structures. The martensitic to austenite transformation temperature decreases with an increase in Ta concentration. Temperature variations of the XRD patterns for the B19 are in reasonable agreement with predicted lattice parameters.

Declaration

I declare that the **Dissertation** hereby submitted to the University of Limpopo, for the degree **Master Science (Physics)** has not previously been submitted by me for a degree at this or any other University; that it is my work in design and in execution, and all material contained herein has been duly acknowledged.



Baloyi M.E (Mr)

20 April 2021

Date

Dedications

This work is dedicated to my lovely grandmother, Patroni Khosa, my sister Tsakani Mavis.

To my brothers, Dennis and Nyikiwa thank you for all the support you have given me during my years of study. My aunty Lilly and Sister in law Martia, you gave me the courage to pursue my dreams. Finally, to God my creator.

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CHAPTER 1

INTRODUCTION

In this chapter, we give a background of the previous theoretical and experimental studies on martensitic shape memory alloys (SMA's). The importance of high temperature shape memory alloys and lastly the objectives and the outline of the current work are given.

1.1. General background

Smart materials are called intelligent materials due to the ability to change with external stimulations and have one or more properties. Smart materials (SM) have been around for decades and they have several applications. When there is a change in the environment, SM exhibit exceptional properties [1]. They have numerous advantages over conventional materials which consist of light-weight, no corrosion, and an increase in the lifespan of the structures that uses them. SM has the ability to impact specific fields which include science, engineering, medicine and automotive industry [2].

Shape memory alloys (SMA) are one of the most famous varieties of type materials and have been the point of interest of intensive research for decades. SMAs are metallic material that has the capacity to recall or preserve their predetermined shape after deformation when heated above certain temperatures [3]. At tremendously low temperatures, those alloys can without problems be elastically or plastically deformed and go back to their original shape upon exposure to some higher temperature. This happens

in two stages, the low-temperature phase known as the martensite and the high-temperature phase referred to as the austenite [4].

Due to their attractive thermal, mechanical properties and high performance in changing heat into mechanical work, SMAs are used to supply high performance actuators and compact damping devices [5]. SMA actuators function effectively and silently, they may be attractive for plenty of engineering applications. The shape memory effect relies on the martensitic transformation (MT). MT is a diffusion-less solid-state transformation from a high temperature parent (austenite) phase to a low temperature (martensite) phase [6]. MT in SMA is exceptionally reversible. Martensitic crystal lattice has a low degree of symmetry than lattice of the austenite.

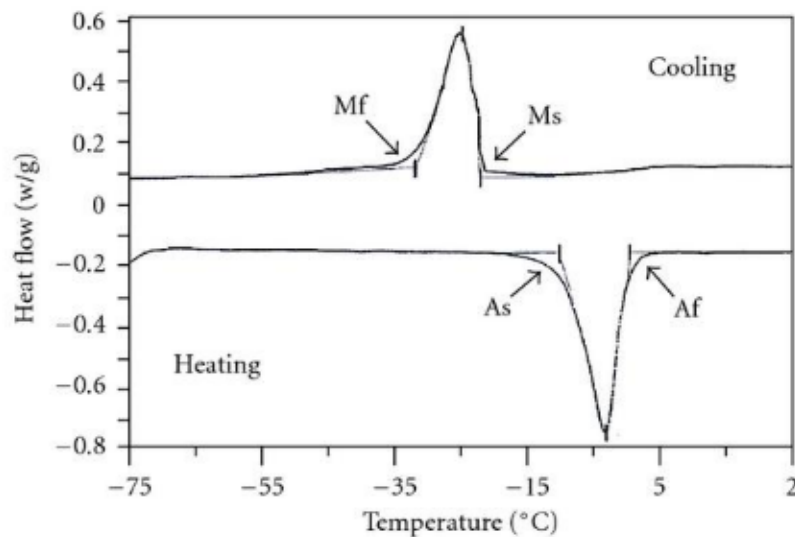


Figure 1. A schematic of a Differential scanning calorimetry (DSC) curve for an SMA showing the phase transformation as peaks and the start and finish of martensite (M_s , M_f) and austenite (A_s , A_f) phases during heating and cooling [7].

Phase transformation occurs over characteristic transformation temperatures particularly martensitic start (M_s), martensitic finish (M_f), austenitic start (A_s) and austenitic finish (A_f).

M_S , M_F , A_S and A_F temperatures are the key parameters governing the thermo-mechanical behaviour of SMAs. In SMA, the austenite phase has an ordered B2 cubic crystal structure as compared to the martensitic phase which has either tetragonal, orthorhombic or monoclinic structures [8]. SMAs are developed for various programs in the automotive, aerospace and medical industries; mainly alloys which indicate a more suitable martensitic transformation temperature. This is because of their specific properties, the shape memory effect (SME) and superelasticity (SE) arising from a solid to solid, diffusionless phase transformation [9].

SME is the capacity of SMAs to return to its original shape of plastically deformed material via heating it [10]. The phase transformation is specifically because of heating which takes place between M_f and A_f . There are different types of SME; One-way SMEs represent a thermal memory, the alloy is deformed at a temperature below A_S . On heating above A_f , all of the martensite variants re-transform back to austenite and the material recovers its authentic shape. Only the shape of the parent phase is remembered using the alloy. Two-way SMEs permits interchanging among extraordinary geometries, especially via temperature alternate. For this effect, special microstructures want to be mounted through precise training treatments, such that a favourably oriented martensite microstructure forms below M_S [11]. If the sample is subjected to training treatment, it is viable for the alloy to remember its parent shape and martensite shape simultaneously. The SME results from non-linear stress recovery upon heating and is used for biomedical and engineering applications. Most of SMA presently used for such kind of applications are restrained to a temperature below 373 K due to their low transformation temperature beneath 373 K, low resistance to excessive temperature oxidation, long-term stability and

low critical stress for slip deformation at high temperatures. Since SME takes place by way of opposite martensitic transformation, martensite transformation temperature governs the operation temperature of SMA [12].

The ability of SMA to recover large strain (~8 %) with related stress-strain hysteresis because of mechanical loading-unloading beneath isothermal situations are referred to as superelasticity. It is an elastic reaction to a carried out pressure, as a result of a phase transformation among the austenitic and martensitic phases of a crystal. It takes place at a temperature above A_f [13]. The stress-induced martensite forms through mechanical loading and the opposite or reverse transformation back to austenite occur on unloading. SE is observed when the martensitic phase transformation is induced by applied thermo-mechanical loading of the austenite phase in which case detwinned martensite is directly produced from austenite. The method is related to large inelastic (transformation) strains which might be advanced upon unloading due to reverse phase transformation [14].

The ability of SMA to reversibly respond to outside temperature changes and change their physical/mechanical properties has enabled them to many applications. SMAs may be used as combined sensors and actuators wherein they could sense the modifications in stimuli and display certain preferred functions [9]. Because of those precise characteristics (SME and SE), SMA has been used as new useful materials for applications which include coupling, sensors, actuators, biomedical, automotive, and aerospace areas. Since the martensitic transformation takes place via a shear-like mechanism, it is possible to set it off even above M_s if the strain is implemented. This is known as stress-induced martensitic (SIM) transformation [15]. The formation of the SIM and its reversion gives an upward push to superelastic behaviour.

1.2. Structural properties of TiM (M = Pt, Ni, Co, Ta)

In this work, we will focus on the 50 % composition of TiM (M: Pt, Ni, Co, Ta) as our parent structure because it exhibits high martensitic transformation. It was reported that B2 TiPt is the high temperature phase with the space group of Pm-3m while B19 is the low temperature phase with the space group of Pmma. The lattice parameters of the B2 TiPt was 3.192 Å. The lattice parameters of the B19 phase at equiatomic composition were $a = 4.55$, $b = 2.73$ and $c = 4.79$ Å [16]. It was reported that TiPt transforms from the high temperature B2 phase to low martensitic phase B19/B19'.

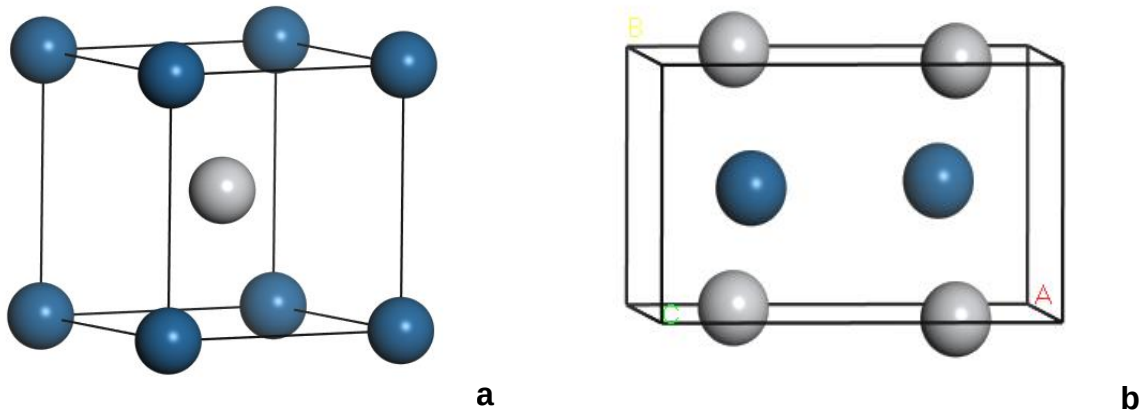


Figure 2. Show the atomic arrangement of (a) B2 and (b) B19 TiPt structures at the equiatomic composition

The addition of Co in the TiPt alloy using the supercell approach may enhance the SME and stabilises the material [17]. TiPtCo ternary alloys have the B19 orthorhombic martensitic phase structure. The lattice parameter of the B2 cubic structure was 3.15 Å at 6.25 at.% of Co with a space group of Pm-3m.

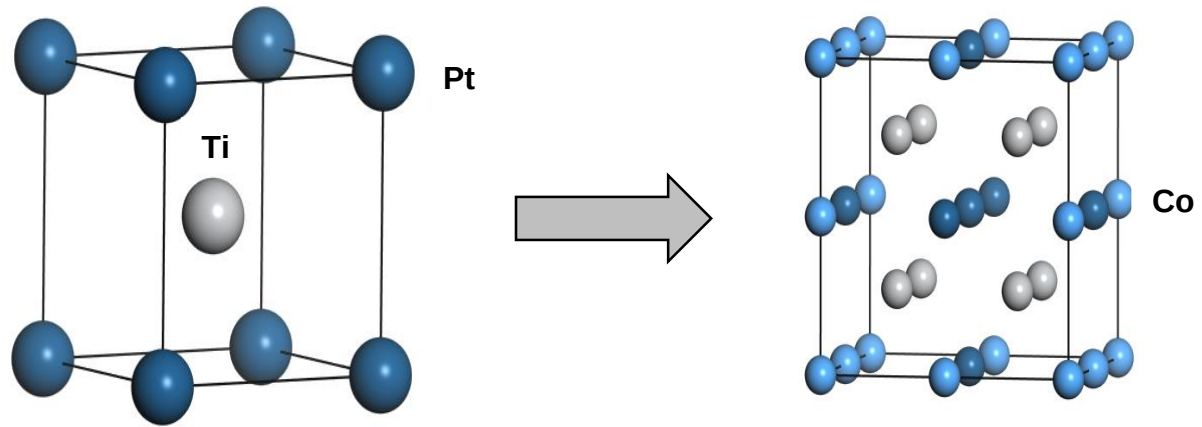


Figure 3. B2 TiPtCo 2x2x2 supercell alloy with 16 atoms.

1.3. The rationale of the study

Shape memory alloys have the capability to remember their shape after being exposed to extreme temperature conditions and deformation, this is due to their shape memory effect (SME) and superelasticity [18]. These alloys have been used in many industrial applications such as aerospace, actuators, and medical fields. HTSMAs are being developed in order to increase the application areas in the aerospace and actuators industries [19]. These alloys could be used for much higher temperature shape memory alloy applications if their shape memory properties can be enhanced by increasing critical stress for slip deformation at high temperature [17].

Recently, many theoretical and experimental studies are being carried out to discover the SMAs properties, particularly features regarding transformation temperature and stability; this phenomenon remains now not well understood [20, 21]. TiPt alloys are a potential candidate for high temperature shape memory applications due to their high martensitic transformation temperature compared to TiAu (897 K) and TiPd (823 K) HTSMAs [22].

However, TiPt alloys have some drawbacks such as instability in the B2 region and negligible shape memory properties. The addition of the third and fourth elements in the TiPt alloy is essential for improving the stability, shape memory properties and high temperature strength [23]. It was reported that the ternary addition of alloying elements such as Zr, Co, Ru, and Cu enhances the shape memory properties but decrease the martensitic transformation temperature.

Here we consider a study on the ternary and quaternary alloying with various elements to enhance the stability, shape memory properties. More importantly, there is a need to maintain high martensitic transformation temperature for TiPt alloy [16]. This is critical for high temperature applications, particularly in the aerospace industry. Despite that the binary TiPt has high transformation temperature, the structure is observed to be unstable [3]. This work employs computational modelling methods to explore the stability, structural and electronic properties of ternary (V, Hf, and Ta) and quaternary (Ta) addition on TiPt alloys, which has the potential to be used for high temperature shape memory applications. Moreover, the method also explores the temperature effect on the B19 and B2 quaternary alloys. Computational modelling includes the ab initio and atomistic simulation, which have shed valuable insights on a wide variety of materials. Ab initio methods tend to be accurate, and confined to a smaller system, whereas Atomistic simulation, on the other hand, enables high temperature studies.

1.4. Aim and objectives

1.4.1. Aim

The aims of the study are to investigate the stability and phase transformation of the Ti-M binary, TiPt-M ternary and TiPtCo-M quaternary shape memory alloys.

1.4.2. Objectives

The objectives of the study are to:

- i. determine the structural and thermodynamic stability, and phase transformation of Ti-M binary, TiPt-M ternary and TiPtCo-M quaternary alloys,
- ii. investigate the electronic density of states,
- iii. determine the mechanical properties i.e. elastic constants,
- iv. determine vibrational stability using phonon dispersion curve,
- v. determine the X-ray diffraction for describing the phase transition of quaternary alloys,
- vi. investigate the effect of temperature of quaternary alloys.

1.5. Outline

In Chapter 1, we dealt with the background on the importance of the SMAs and Ti-based alloys. Chapter 2 gives a detailed literature review on Ti-based alloys and other related SMAs. We briefly summarised the importance and uses of these alloys, which has been achieved previously in both experimental and computational approaches.

In Chapter 3, we discuss the theoretical techniques that are used to perform the calculations of the B2 TiM (M=Pt, Ta, Co, Ni), $\text{Ti}_{50}\text{Pt}_{50-x}\text{M}_x$ (M = Ta, V, Hf) and $\text{Ti}_{50}\text{Pt}_{43.75-}$

$x\text{Co}_{6.25/18.75}\text{Ta}_x$ systems. The density functional theory and plane-wave pseudopotential methods are summarised.

In Chapter 4, we present the DFT results generated in this study. We discuss the B2 TiPt phonon dispersion spectra emanating from soft modes. The phases are optimized and their equilibrium lattice parameters, heats of formation, phonon dispersion curves and density of states are also discussed.

In Chapter 5, we present the equilibrium lattice parameters and heats of formation of the $\text{Ti}_{50}\text{Pt}_{50-x}\text{M}_x$ to deduce the structural stability. We also discuss their mechanical properties, phonon dispersion curves and density of states.

Chapter 6 is concerned with quaternary alloys. We use the supercell approach to generate various compositions of the B2 $\text{Ti}_{50}\text{Pt}_{43.75-x}\text{Co}_{6.25}\text{Ta}_x$, B19 $\text{Ti}_{50}\text{Pt}_{43.75-x}\text{Co}_{6.25}\text{Ta}_x$ and B19 $\text{Ti}_{50}\text{Pt}_{31.25-x}\text{Co}_{18.75}\text{Ta}_x$ quaternary alloys. Their heats of formation, elastic constants, phonon dispersion curves and the temperature effect in terms of lattice expansion and X-ray diffraction patterns are discussed.

Chapter 7 give the summary and the conclusion of our study. Finally, the references for the study are listed.

CHAPTER 2

LITERATURE REVIEW

In this chapter, we give a short-lived review of the previous theoretical, experimental and some computational studies on binary, ternary and quaternary Ti-based shape memory alloys (SMA).

2.1. Ti-based alloys

Titanium-based SMAs have attracted huge attention due to their one-of-a-kind properties, shape memory effects and superelasticity for wide range of applications in the field of engineering and medicine, which can be displayed in martensitic transformation [16]. Titanium (Ti) and its alloys, owing to their high strength to weight ratio and high temperature properties, are used extensively by the aerospace industry. The same properties make them useful for the production of gas turbine engines, particularly for parts such as the compressor blades, casings, engine cowlings and heat shields [24, 25].

Excellent cold-workability of β Ti-based SMAs have made them attractive for practical application as new smart materials since they can be easily fabricated to fine wires and thin plates of dimensions suitable for actual application [21]. However, they are very sensitive to aging above 373 K where ω phase forms during aging, which decrease the M_s Temperature or completely overturn shape memory effect. To increase the application temperature of β Ti-based SMAs to temperature above 373 K, it is crucial to suppress the formation of ω phase by addition of alloying element [26]. The alloying elements of Ti are

categorized as α -stabilizer (Al, O, N, and C), β -stabilizer (Mo, V, Ta, Nb, Fe, Ni, Mn, Cu, Cr, Si, and H) and neutral elements (Sn and Zr) [15].

It is widely known that most Ti-based SMAs have an ordered B2 phase at high temperatures and transform to a low temperature martensitic phase (B19/B19') upon cooling [19]. These martensitic alloys designate an important group of innovative materials which exhibit unusual properties. The unique properties of SMA expand from the crystallographically reversible martensitic transformation among the parent phase and martensite phase. The martensitic transformation temperatures are great on account that they describe the restriction temperature of SMAs applications [27].

Nickel Titanium (NiTi) is one of the most studied SMAs and due to their desirable mechanical properties [28], it leads the growing marketplace as compared to other SMAs [29]. Also, titanium cobalt (TiCo), titanium zirconium (TiZr), titanium tantalum (TiTa) and titanium platinum (TiPt) are some of the alloys that have been studied extensively [30, 31, 3, 32]. TiCo alloys are extensively applied in biomedicine due to their tremendous biocompatibility, high corrosion resistance and low density [33, 34]. The transformation temperature of TiCo is about 40 K and undergoes a B2 to B19' martensitic transformation. In addition, TiZr and TiTa are also used in biomedical applications [32, 35]. TiZr possesses advantages which include low cost and suitable plasticity [36]. Its transformation temperature was reported to be around 871 K [37]. TiTa alloys had been proposed as one of the high-quality choices for biomedical applications [35, 38] due to their extraordinary biocompatibility in human body environment, excessive strength, particularly low elastic moduli and enhanced corrosion resistance [31]. Martensitic start,

$M_s = 440\text{ K}$ [39], this high value of M_s makes TiTa appealing as the base system for the development of new high temperature SMA.

Recently there is a growing demand for SMAs that can be used at high temperatures [16]. Nitinol has limited applications because of its low martensitic transformation temperature less than 373 K [40] and is considered as a low temperature SMAs. Although they have been studied for over half a century, new applications continue to be developed for SMAs [24]. There has been ternary alloying on the NiTi to increase shape memory properties and transformation temperatures, ternary alloys such as NiTiCu, NiTiPd, NiTiAu and NiTiPt [21, 41]. The transformation temperature of NiTiPt was reported to be higher than that of NiTi [42] and shape memory properties occur at higher temperatures [43]. B19 is observed in ternary alloys of NiTi, for NiTiCu the transformation behaviour changes from B2-B19' to B2-B19 with increasing Cu content material [44]. This indicates that the transformation temperature of NiTi increases significantly [16]. However, it is limited to certain temperatures. Moreover, TiCoPt ternary alloys are suggested by Hu et al [30] to enhance the overall performance of the TiCo alloy and transformation temperature occurred at 1173 K [30, 45]. The existence of the ternary phase τ was observed with composition ranging from 23.6 to 29.9 at.% Pt at 973 K and from 27.4 to 40.1 at.% Pt at 1173 K [30].

A few B2 stabilizers were added into TiZr and TiTa binary alloys to increase the B2 phase stability and enhance the SME [31, 32]. The β -phase transformation temperature increases progressively with the increase of Al content, the transition temperature from α to β for TiZr-5Al was found to be 1111 to 1167 K [32]. TiTa alloys were observed appealing as a base system for the development of new HTSMAs and advanced actuators

applications because of their exceptionally high transformation temperatures [46, 39, 47]. However, TiTa has poor shape memory properties as compared to TiNi which needs to be improved as suggested by Ning et al [48]. Development of SMAs that can operate at high temperature is ongoing, mainly to increase the application areas and shape memory properties. TiPt occurs in numerous phases, particularly B2, B19 and B19' phases [16]. TiPt exhibit a thermos elastic orthorhombic (B19) martensitic phase transformation from austenite (B2). High and low temperature phases had been identified as B2 and B19 structures using high temperature X-ray diffractometry, so martensitic transformation in TiPt was considered [16].

TiPt is a promising high temperature SMA due to its high transformation temperature of around 1300 K [49] as a binary. It undergoes a B2-B19 martensite phase transformation at 50:50 at.% composition with a transition temperature of approximately 1323 K [50, 51, 16] and this can be observed on the Ti-Pt phase diagram shown in Figure 4 [52]. The mechanical and elastic properties of TiPt alloys have been investigated previously [3] within the density functional theory (DFT) and the stability trend is in the order $B2 < L1_0 < B19' < B19$. The B2 phase is reported to be highly unstable at 0 K with respect to the heats of formation whereas the B19 is more stable. Elastic constants of the B19', B19, and L1₀ are satisfying the stability criteria with positive values. The shear modulus C' of the cubic B2 value is negative which implied the instability of the phase at 0 K. The densities of states (DOS) for the structures were also determined and B2 was unstable with the highest number of DOS at the Fermi level as opposed to the B19 which had low DOS. The B2 showed that it is indeed the high temperature phase as it is unstable with

respect to the mechanical properties investigated whereas B19 is the lower temperature phase.

The experimental work on the equiatomic Ti-Pt based alloys suggested that the phases exhibit very low shape memory effect attributed to low critical stress for slip deformation compared to the stress required for martensitic transformation [51, 16]. Therefore, there is a need to improve the mechanical properties of the alloys for them to be used at higher temperatures [20]. TiPt has the potential to be used for much higher temperature applications in comparison to TiAu and TiPd HTSMAs [22].

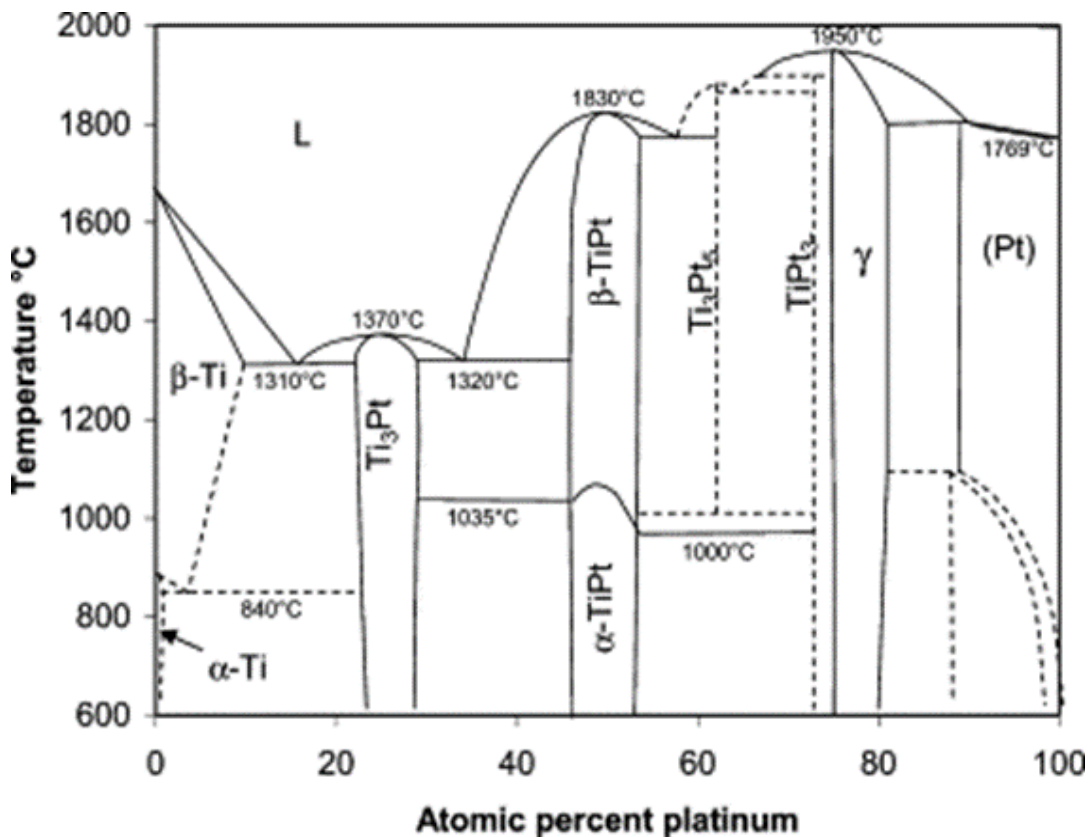


Figure 4. Ti-Pt phase diagram. The area of interest is around 50 at.% Pt where the low-temperature α -TiPt (B19) phase and the high-temperature β -TiPt (B2) phase exist [52].

Ternary alloying on the Ti-Pt has been recommended to enhance the mechanical properties of these alloys [3]. In recent studies, attempts to develop and improve the stability and shape memory properties of TiPt alloys are being taken by ternary alloying [49]. Wadood et al [17] investigated the ternary alloying of TiPt with Co, Zr, Hf and Ru. The addition of Ru and Co was found to be decreasing the transformation temperature of TiPt [22] alloy. Moreover, the work reported on the addition of Co on the TiPt by Mahlangu et al [53] using density functional theory suggested a decrease in transformation temperature in agreement with the experiments [22].

B2 $\text{Ti}_{50}\text{Pt}_{50-x}\text{Co}_x$ (6.25, 18.75 and 25 at.%) was reported to be mechanically stable with all C_{ij} 's being positive, satisfying cubic stability criteria [53]. At low content of Co (6.25 at.%) B2 to B19 transformation takes place because it has large anisotropy of approximately 4.67 and at high content of Co (18.75 and 25 at.%), the shape undergo B2 to B19' martensitic transformation [17]. Compressive strength of TiPt in martensitic phase was increased by partial substitution of Pt with Co and Ru which also act a B2 stabilizer. Furthermore, TiPt-Co ternary alloys have insignificant strength at high temperature conditions and it is found to be vibrationally unstable [54, 55] since there are vibrations observed in the negative frequency as suggested by the phonon dispersion curves. B19 $\text{Ti}_{50}\text{Pt}_{43.75}\text{Co}_{6.25}$ predicted the highest martensitic transformation temperature from B19 to B2 at 1473 K to 1673 K [53].

High temperature strength and shape memory properties of TiPt have been improved via partial substitution of Pt with Ru, Zr, Hf and Co atoms. Zr, Co and Hf are the most effective alloying elements that enhanced shape recovery ratio between 40-60% [17]. Zr and Hf are the actual strengthening alloying elements compared to Co and Ru in TiPt system for

higher shape memory recovery [49]. Compressive strength at 50 K below M_f of Ti-50Pt-5Zr (1468 MPa) and Ti-45Pt-5Ru (711 MPa) was much higher than that of TiPt (485 MPa) alloys. It is concluded that these Ti-50Pt-5Zr and Ti-45Pt-5Ru advanced alloys have the capability for high temperature materials applications [43]. However, ternary alloying on TiPt has few drawbacks, transformation temperatures have been decreased by using partial substitution of Pt with Zr, Hf and Ru [49]. Moreover, Chikosha et al stated that vanadium addition to TiPt has a negligible effect on the martensite to austenite transformation temperatures, where the addition of 6.25 at.% V reduces the martensitic transformation (from $M_s = 1247$ K to $M_s = 1162$ K) of the alloy [56].

Chauke et al stated that the thermodynamic stability of ternary structures favoured Co and Zr in B2, and Ir in B19 doped system [54]. The martensitic transformation temperature of the $Ti_{50}Pt_{43.75}Pd_{6.25}$ and $Ti_{50}Pt_{43.75}Zr_{6.25}$ was lower, with Pd doped starting from 873 K to 973 K; and 6.25 at. % Zr starting at 673 K to 1273 K. This observation indicates that Zr may additionally select the Ti sub-lattice than Pt as mentioned in literature while Pd might also stabilise at high concentrations above 20 at. %. It was observed that $Ti_{50}Pt_{45}Ru_5$ to be the most stable with expansion as compared to $Ti_{50}Pt_{45}Zr_5$ and $Ti_{50}Pt_{45}Hf_5$. Moreover, B19 $Ti_{50}Pt_{45}Co_5$ gave rise to Co being the most mechanically stable ternary structure [57].

Addition of Ir to TiPt is expected to increase the martensitic transformation temperature because Ir has a high melting temperature (2739 K) compared to Ti and Pt atoms. Transformation temperature increased by Ir addition and was found to be 1491 K in Ti-12.5Pt-37.5Ir. Strain recovery of 1.7 % and shape recovery ratio of 57 % become acquired in Ti-25Pt-25Ir after deformation at 1123 K. All transformation temperatures expanded with increasing Ir content. Shape recovery and superelasticity were observed in the

ternary Ti-Pt-Ir, and this shows that Ir addition is powerful in improving the SME [58]. However, all of the independent elastic constants are positive except for C' (-2.5) which is negative for Ir doped system (regarded as mechanically unstable) [54]. Furthermore, Ir additions were found to possess a negligible effect on the shape recovery ratio [22].

Some quaternary shape memory alloys have become potential candidates for high temperature SMA such as TiNiPdCu, NiTiHfCu, NiTiHfZr and NiTiHfTa SMAs [59]. Moreover, quaternary NiTiHfPd display outstanding stability. $\text{Ni}_{45.3}\text{Ti}_{29.7}\text{Hf}_{20}\text{Cu}_5$ has a transformation temperature above 373 K which qualifies this alloy as high temperature SMA [60]. The phase transformation of $\text{Ti}_{36}\text{Ni}_{46}\text{Hf}_{15}\text{Cu}_3$ alloy were found to be $M_f = 402$ K, $M_s = 416$ K, $A_s = 471$ K, $A_f = 490$ K and those of $\text{Ti}_{36}\text{Ni}_{44}\text{Hf}_{15}\text{Cu}_5$ alloy $M_f = 424$ K, $M_s = 435$ K, $A_s = 488$ K, $A_f = 506$ K [23]. Quaternary alloys such as TiNiPdCu has been found to possess high transformation temperatures of 773 K and are stable at high temperature [47].

Despite that the binary TiPt has a high transformation temperature, the structure is observed to be unstable [3]. The ternary TiPtCo has an enhanced shape recovery ratio [17] and high transformation temperature [53], but it is observed to be unstable. Moreover, there is limited study on TiPt-based quaternary alloying. In the present study, quaternary alloying with metal such as Tantalum (Ta) have been suggested due to its high melting temperature [53], as an alternative to enhance the stability, shape memory effect and transformation temperature of TiPtCo ternary alloys. This work will give insights into the stability of TiPt and TiPtCo-Ta alloys high temperature applications.

2.2. Background on the properties to be investigated

Ab initio calculations refer to an approach in which properties of materials may be determined using quantum mechanical techniques. Some of these properties include heats of formation, elastic properties, phonon dispersions and density of states which will be reviewed below as they are appropriate for the current study.

2.2.1. Heats of formation

The heats of formation (ΔH_f) and associated entropies offer essential information on stabilities of the compound and in constructing their phase diagrams. Bennett-Watson's model approach is crucial to predict the enthalpy of formation of the metal compound at equiatomic composition [61]. ΔH_f of a compound is well-described as the change in enthalpy at room temperature amongst the compound and its fundamental elements in their standard state [62]. The standard ΔH_f of a compound is the change of enthalpy that accompanies the formation of one mole of a substance in its standard state from its composite elements in their standard states (1 bar and 298 K). ΔH_f is estimated by [63];

$$\Delta H_f = E_c - \sum_i x_i E_i, \quad (1)$$

where E_c is the calculated total energy of the compound, E_i is the calculated total energy of the element i in the compound and x_i is the composition of each element. A small difference in the ΔH_f among the austenite and the martensite suggests that the B2 structure is not that unstable relative to the low-temperature phase and may hence survive to a lower temperature, leading to a lower martensite start (M_s) temperature. M_s is also correlated with the heats of formation of the B2 phase such that the alloy with a larger B2 phase has a higher heats of formation [41]. The lowest value of ΔH_f suggests

the stability of the phase whereas the highest value is associated with the instability of the alloys.

Baloyi et al reported on the stabilities of binary TiPt, TiCo, TiNi, TiTa and TiZr by calculating their heats of formation, TiPt was found to be the most favourable binary alloy due to its lower heats of formation value [18, 64]. Moreover, the stability of TiPtCo [53] and TiPtM (M = Ru, Co, Cu, Zr, Hf) [57] ternary alloys was also investigated. We can also use heats of formation to investigate the stability of the alloys under study.

2.2.2. Elastic constants

Elastic constants are a reaction function to the external forces and are of huge importance in materials properties [65]. In material science, the wide variety that quantifies the response of a specific material to elastic or non-elastic deformation while a strain load is implemented to that material is referred to as elastic constants (EC). EC has a relationship with dynamical matrix [66] within the theory of elasticity, which can be associated with the phonon frequencies which in turn have a connection with the atomic force constants via discrete nature of substances. However, EC can be used to distinguish elastic from plastic regimes by using elastic stability criteria [67].

The elastic property is amongst the most vital physical properties of materials. EC consists of a number of the more important information that may be obtained on the ground-state total energy calculations. First principle studies at the elastic properties of SMAs are important to well understand their martensitic transformation behaviour [21]. The ECs include a quite facts about the stability and offer a tool to obtain mechanical properties of solids such as strength, hardness, Voigt's modulus, Reuss's modulus, Hill's modulus, shear, Young's, bulk modulus, elastic stiffness coefficients, Poisson's ratio and

melting temperature. Phonon dispersion spectrum and phonon density of states are associated with the ECs as well [68].

The elastic constants are significant properties inclusive of structural stability and phase transition of metal alloy materials. The calculation of bulk properties which includes lattice parameters and heats of formation is much less complex as compared to the ab initio calculation for the determination of elastic constant [3]. The alloying and temperature effects of the system must be considered in the calculations on the total energy because the elastic constants depend much greater on the structure of the alloy and the ambient temperature. The calculated C_{ij} can be used to check the bulk and shear moduli and to calibrate model calculations. To understand the martensitic transformation of alloys, elastic properties are considered [21]. For a cubic material, there are three independent elastic constants (C_{11} , C_{12} , C_{44}). The stability criterion for the cubic system to be mechanically stable was reported previously [3].

Phasha et al reported on the elastic moduli which are calculated based on the three independent elastic constants [69]. To improve the mechanical durability of materials, the elastic anisotropy factor (A) [70] is calculated. Higher A is a sufficient condition for high transformation temperature, B2 to B19 while lower A for low transformation temperature to B2 to B19'. If the value of A is 1, the material is taken into consideration elastic anisotropic (less micro-crack inside the material) and when is smaller or larger than 1 measure the degree of elastic anisotropy [3]. The elastic constant is currently used to deduce the mechanical stability of the structures. Chang-Long et al reported on the stability of binary alloys [21] while Mashamaite et al reported on the ternary alloys [57]. We can also deduce the stability of the alloys using an elastic constant.

2.2.3. Phonon dispersion

Phonon is a quantum mechanical description of essential vibrational movement wherein a lattice of atoms or molecules uniformly oscillates at a single frequency. They play a critical role within the physics of the solid-state and govern the thermal properties in semiconductors and insulators. Their impact on thermal, electric, optical and different properties of bulk materials is important. ECs and the phonon dispersion are directly related to each other; EC is proportional to the slopes of the linear low frequency acoustic phonon modes which can be linear in wave vector [68].

Comprehensive understanding of lattice vibrations is critical for the understanding and quantitative prediction of a huge variety of physical properties of solids [71]. Phonon dispersion curves along specific high symmetry directions in reciprocal space were determined to employ the approach of interplanar force constants, where planes perpendicular to these directions are displaced within an elongated supercell [72]. They predict the stability of SMAs through the vibration of atoms. Phonons are allowed vibrational modes in solids and energies of these lattice vibrations are quantized due to the fact only certain modes of vibrations are allowed. Dispersion relation in metals is typically taken into consideration on the speculation that the interatomic forces have a fairly short range. The behaviour of the phonons within the crystal is only modelled inside one Brillouin zone [73]. Each Brillouin region shows one unit cell in reciprocal space. If the Brillouin zone comprises of multiple atoms, then two different modes of phonons transpire, particularly the acoustic mode and the optical mode.

Vibrational density of states (DOS) or phonon DOS is the measure of phonon distribution in a material [74]. It gives information about the energy of the specific phonons in the

materials and may be used to pick out the dominant phonon. The special techniques for ab initio evaluation of vibrational properties have been developed, namely, analytical calculation of force constants based on a perturbative expansion around the equilibrium geometry and Fourier transform of the atomic velocity autocorrelation function obtained from a molecular dynamics trajectory [75]. Localized travelling waves of atomic vibrations in solids, referred to as phonons, are quantized with the energy $\hbar\omega = \hbar v$, where $v = \omega/2\pi$ is the frequency of vibration of the wave [68].

The dispersion relations exhibit two types of phonons namely the optical and acoustic modes corresponding to the upper and lower sets of curves in the diagram, respectively. The lower branch is called acoustic mode when k is insignificant the dispersion curve is of the shape $\omega = vk$. The acoustic mode tallies to sound waves travelling via the crystal. The upper branch is known as optical modes that are responsible for the optical behaviour of solids [76]. The optical mode interacting either directly or indirectly with light [77]. Phonon modes are categorized in a couple of methods, in particular, 3 of these modes are called acoustic modes. A mode is acoustic if its energy vanishes as $\vec{q} \rightarrow 0$, these modes are gapless. Amongst the 3 acoustic modes, one is longitudinal and two are transverse modes, where the atoms are displaced perpendicular to $\vec{q}$ when $q \rightarrow 0$ [78]. Acoustic is activated whilst sound propagates via the crystal and these acoustic phonons are also called Goldstone modes. The Goldstone theorem states that each time the system breaks a continuous symmetry, there may be a gapless boson associated with that [79]. For extra complex crystals with $r \geq 2$, the closing $3(r - 1)$ modes are referred to as optical modes. These are gapped modes.

The MedeA-Phonon module is based on the general direct approach to lattice dynamics and is designed to work independently of a particular underlying code for deriving forces and general energies [80]. However, collectively with the VASP, a fully automated and high parallel procedure is provided within MedeA. Structures are said to be stable if and only if there are no observed soft modes in the negative frequency in the phonon dispersion curve, otherwise it is considered to be unstable. Moreover, the B2 TiPt and TiNi were reported to be vibrational unstable [20].

2.2.4. Electronic density of states

The density of states (DOS) is a beneficial mathematical idea allowing integration concerning the electron energy for use instead of the integration over the Brillouin zone. DOS offers the number of electronic states which are available in the system per volume at given energy [81]. Electronic states encompass localized impurity states and delocalized conduction and valence band states. The states within the band and their energy dependence are defined through the DOS. Knowledge of band structure and Fermi level of intermetallic compounds is crucial to the concepts of alloy phase stability. Moreover, the DOS for conduction and valence bands relies upon the available states for occupation and occupancy probability at that energy. The general distribution of states as a function of energy and spacing among energy bands in semiconductors can be determined from the DOS calculations [82].

More accurate strategies are primarily based on linear or quadratic interpolations of band energies among reference factors in the Brillouin zone. High DOS at a selected energy level means that there are numerous available states for occupation while DOS of zero means no states available for occupation at that energy level [83]. DOS appears in many

physics and help to explain several quantum mechanical phenomena. It is significant to calculate DOS of particles while investigating the thermodynamic properties of the system.

Besides, the DOS is frequently used for brief visual evaluation of the electronic structure. Characteristics consisting of the width of the valence band and the energy gap are helpful in qualitatively interpreting experimental spectroscopic information. DOS evaluation can also assist to apprehend the adjustments in electronic structure because of external pressure [82].

The most popular and reliable approach, that is primarily based at the tetrahedron interpolation, is regrettably ill-suited to the Monkhorst-Pack grid of unique factors. Therefore, VASP makes use of a simplified linear interpolation scheme [84]. This technique is based on the linear interpolation in parallelepipeds formed by way of the points of the Monkhorst-Pack set, followed with the aid of the histogram sampling of the consequent set of band energies.

DOS behaviour at E_f is significant and can be used to correlate the stability of the materials. It is also known from the literature that the DOS of structures of the same composition can be used to mimic the stability trend with respect to their behaviour at the E_f [21]. DOS is used to predict the stability of metals alloys. The structure with the highest and lowest density of states at E_f is considered the least and most stable, respectively. If the Fermi level E_f falls on the pseudogap, the corresponding structure may be regarded as a save energy system as compared with one which Fermi level E_f does not fall on pseudogap. Moreover, the electronic stability of TiPt phases was reported by deducing

their DOS [21, 3] and this shows that we can use this property to deduce the stability of the structures.

CHAPTER 3

METHODOLOGY

3.1. Introduction

In this chapter, a brief assessment of the theoretical background of methodologies used in this study is presented. Our approach is based totally on the quantum mechanical calculations that are the density functional theory (DFT). Since quantum mechanical methods are widely used to study the structural, electronic, elastic and vibrational properties of the materials. The code employs a plane-wave technique to deal with susceptible pseudopotentials and capable of simulating electronic relaxation to the ground state for metals.

To study the properties of the materials, we employ computational codes such as VASP, CASTEP and LAMMPS. The VASP code embedded in MedeA is used to calculate the ab initio properties such as structural, electronic, elastic and vibrational to deduce the stability of the material. Moreover, the molecular dynamics calculation are carried out using the computational code known as LAMMPS to calculate the effect of temperature on quaternary alloys whereas CASTEP embedded in the material studio is used to calculate the X-ray diffraction for describing phase transition of quaternary alloys.

3.2. Density functional theory

Density functional theory (DFT) is one of the most famous and successful quantum mechanical approaches used to study ground states properties of systems [85]. DFT was formulated by Hohenberg-Kohn [86] and Kohn-Sham [87] six decades ago to provide the foundation for accurate calculations. While the Schrödinger equation (SE) is hardly doable analytically, numerical processes to acquiring approximate solutions for the electronic structure have become invaluable to chemistry and material science. The Kohn-Sham (KS) equations are equivalent to the Schrodinger equation (SE). The larger and more realistic model system can be studied since the KS equation can be solved significantly faster than the SE in most cases [88].

In 1964, Hohenberg and Kohn [86], and Kohn and Sham [87] reformulated the SE to involve all of the $3N$ spatial coordinates of N interacting electrons, an idea based on the electron density, a feature of simplest 3 spatial coordinates. DFT is a widely-used technique as it is computationally more efficient than different quantum techniques with similar accuracy and it gives a quantum-mechanical basis for most of the ab initio strategies utilized in computational material science [89]. In DFT, the total electron density is decomposed into one-electron densities,

$$E = E(\rho), \quad (2)$$

which are constructed from one-electron wave functions.

The idea of using the electron density as the fundamental entity of a quantum mechanical theory of matter originates in the early days of quantum mechanics in the 1920s, especially by the work of Thomas [90]. However, in the subsequent decades, it was rather

the Hartree-Fock approach [91], which was developed and applied to small molecular systems. Calculations on realistic solid state systems were then out of reach. In 1951, Slater [92] used ideas from the electron gas intending to simplify Hartree-Fock theory to a point where electronic structure calculations on solids became feasible [93]. The electron density is a scalar quantity within the solid-state systems, molecules and atoms described at each point r in real space as,

$$\rho = \rho(r). \quad (3)$$

The total energy of the system is decomposed into three terms, kinetic energy, coulomb energy and the exchange-correlation energy that captures all many body interactions,

$$E = T_0 + U + E_{xc}. \quad (4)$$

T_0 is the sum of the kinetic energies of all effective electrons and E_{xc} is the exchange-correlation energy. The most straightforward term is the Coulomb energy U . It is purely classical and contains the electrostatic energy arising from the Coulomb attraction between electrons and nuclei, the repulsion between all electronic charges and the repulsion between nuclei,

$$U = U_{en} + U_{ee} + U_{nn} \quad , \quad (5)$$

with

$$U_{en} = -e^2 \sum_{\alpha} Z_{\alpha} \int \frac{\rho(r)}{|r - R_{\alpha}|} dr \quad , \quad (6)$$

$$U_{ee} = e^2 \iint \frac{\rho(r)\rho(r')}{|r - r'|} dr dr' \quad , \quad (7)$$

$$U_{nn} = e^2 \sum_{\alpha\alpha'} \frac{Z_\alpha Z_{\alpha'}}{|R_\alpha - R_{\alpha'}|}, \quad (8)$$

where e is the elementary charge of a proton and Z_α is the atomic number of an atom α . U_{en} is the Coulomb energy between an electron and nuclei, U_{ee} is the Coulomb energy between two electrons whereas U_{nn} is between two nuclei. The summations extend over all atoms and the integrations overall space.

The second Hohenburg-Kohn (HK) theorem state that the ground-state electron density may be calculated exactly using the vibrational method. This principle is carried out to determine the electron density from which the total energy of the ground state is calculated. The KS equations are defined as

$$\left[-\frac{\hbar^2}{2m} \nabla^2 + V_{eff}(r) \right] \psi_i(r) = \varepsilon_i \psi_i(r), \quad (9)$$

with

$$V_{eff}(r) = V_c(r) + \mu_{xc}[\rho(r)]. \quad (10)$$

where $V_c(r)$ is the external potential and $\mu_{xc}[\rho(r)]$ is the exchange-correlation density functional [94]. The electron density, which corresponds to these wave functions, is the ground state density which minimizes the total energy. Therefore, the KS total energy functional can be expressed as [95]:

$$E = \frac{1}{2} \sum_{occ} \varepsilon_i + U_{nn} - \frac{e^2}{2} \iint \frac{\rho(r)\rho(r')}{|r-r'|} dr dr' + E_{xc}[\rho(r)] - \int \rho(r) \mu_{xc} dr. \quad (11)$$

The variational principle state that a trial value greater than (or equal to) its lowest possible value:

$$E[\rho'] \geq E_0[\rho], \quad (12)$$

where ρ and ρ' are the ground state energy and any trial density satisfy the boundary conditions $\rho'(r) \geq 0$, $\int \rho(r)dr = N$, with the corresponding ground-state energy E_0 and any trial energy E , respectively. The exchange-correlation energy is depending on the electron density. In practice, however, the exchange-correlation energy (and thus the exchange-correlation potential) is not known and one has to make approximations which will be discussed in the next section.

3.3. Approximation methods

The functional is the part of the transformation of the SE external potential into the KS effective potential. Approximations need to be used since the exact functional to give the same answer as the SE for the ground state is not available. Approximate functionals, such as local density approximation (LDA), generalized gradient approximation (GGA), meta-generalized gradient approximation (meta-GGA) and hybrids, give reasonably accurate outcomes.

3.3.1. Local density approximation

The simplest approximation is to assume that at each point in space, we will use the value of density that the uniform electron gas would have at that point and permit it to differ from point to point. Local density approximation (LDA) gives the correct sum rule for the exchange-correlation hole [96]. LDA makes use of most effective the electron density, $\rho(r)$, at spatial point r to determine the exchange-correlation energy density at that point. This can be written as

$$E_{XC}^{LDA}[\rho] = \int \rho(r) \epsilon_{xc}^0[\rho(r)] dr, \quad (13)$$

$$\varepsilon_{xc}(\rho(\vec{r})) = \varepsilon_x(\rho(\vec{r})) + \varepsilon_c(\rho(\vec{r})), \quad (14)$$

where

$$\varepsilon_x(\rho(\vec{r})) = -\frac{3}{4} \left(\frac{3\rho(\vec{r})}{\pi} \right)^{1/3}, \quad (15)$$

$\varepsilon_x(\rho(\vec{r}))$ is the Dirac-Slater Exchange Energy of the electron gas. All modern LDA correlation functionals are based on 1980 Monte Carlo calculation of the total energy of the uniform electron gas. Lattice parameters expected with the LDA are too short, weak bonds are remarkably too short and the binding energies are normally too big. The LDA amounts to the following picture: at each point in a molecule or solid there exists a well-defined electron density; it is assumed that an electron at such a point experiences the same many-body response by the surrounding electrons as if the density of these surrounding electrons had the same value throughout the entire space as at the point of the reference electron. The exchange-correlation energy of the total molecule or solid is then the integral over the contributions from each volume element [97].

This approximation was found to reproduce the ground-state properties of many systems with fairly high accuracy. LDA is critical in the construction of greater refined approximations to the alternate-correlation energy, along with generalized gradient approximations or hybrid functionals [98].

3.3.2. Generalized gradient approximation

Gradient-corrected density functionals as suggested by Perdew [99], Becke [100], Perdew and Wang [101] and Perdew, Burke and Ernzerhof [102] offer a remedy to the LDA discussed above. The basic idea in these schemes is the inclusion of terms in the exchange-correlation expressions that depend on the gradient of the electron density and

not only on its value at each point in space. Therefore, these corrections are also sometimes referred to as "non-local" potentials. The generalized gradient approximation (GGA) was introduced to improve some of the LDA weaknesses [103]. It is vital to encompass terms that explicitly recall the spatial variation of the density. The good accuracy density functional theory is made viable by using a formulation of functionals in the GGA. The improvement of GGA indicates agreement with the experiments for properties of the finite system inclusive of atoms or molecules. The gradient correction to the total energy for exchange by Becke, and the correlation through Perdew [104],

$$E_{GGA} = E_{LDA} + E_X^G + E_c^G, \quad (16)$$

with

$$E_x^G = b \sum_{\sigma} \int \frac{\rho_{\sigma} x_{\sigma}^2}{1 + 6b x_{\sigma} \sinh^{-1} x_{\sigma}} dr, \quad (17)$$

$$x_{\sigma} = \frac{|\nabla \rho|}{\rho_{\sigma}^{4/3}} \quad \sigma = \uparrow \text{ or } \downarrow,$$

$$E_c^G = \int f(\rho_{\uparrow} \rho_{\downarrow}) e^{-g(\rho) |\nabla \rho|} |\nabla \rho|^2 dr. \quad (18)$$

The gradient introduces non-locality into the account of exchange and correlation. These functionals are all local within the mathematical sense however move beyond the local density approximation [102].

The use of GGA has little influence on local properties and tends to overestimate the bond lengths and cell parameters, but does lead usually to a significant improvement in global changes in the total energy, such as those that result when two atoms combine to make

a molecule. In this work, we used the PBE form of the GGA [99], which was designed to be more robust and accurate than the original GGA formulation [101].

3.4. Planewave pseudopotential method

3.4.1. Pseudopotentials

The pseudopotential approximation allows the electronic wavefunctions to be expanded using a much smaller number of plane-wave basis states. A decade ago, the success of DFT in the prediction of materials properties branches in large part from the pseudopotentials (PPs) application. PPs decreases the variational degree of freedom and evades the numerical encounter of immediate spatial variations within the electronic structure. The pseudopotential approximation allows the electronic wave functions to be multiplied using a much smaller number of plane wave basis states [105].

The valence wave functions oscillate hastily in the region engaged by way of the core electrons due to the strong ionic potential in this region, which preserves the orthogonality between the core wave functions and the valence wave functions, which is required in Pauli's exclusion principle [106]. The pseudopotential is constructed in such a way that its scattering properties or phase shifts for the pseudo wavefunctions are identical to the scattering properties of the ion and the core electrons for the valence wavefunctions, but in such a way that the pseudo wavefunctions have no radial nodes in the core region. The phase shift produced by the ion core is different for each angular momentum component of the valence wave function and so the scattering from the pseudopotential must be angular momentum dependent. The most general form for pseudopotential is

$$V_{NL} = \sum_{lm} |l_m\rangle V_l \langle l_m|, \quad (19)$$

where $\langle l_m |$ are the spherical harmonics and V_l is the pseudopotential for angular momentum l . Local pseudopotential makes use of the identical potential for all the angular momentum components of the wave characteristic. A pseudopotential that uses the same potential for all the angular momentum components of the wave feature is called a local pseudopotential. Without a smooth, weak pseudopotential it will become tough to increase the wave functions using a reasonable number of plane wave's basis states [107].

3.4.2. Plane wave basis and plane wave pseudopotential

The plane wave pseudopotential approach has become one of the most widely used techniques for calculating the ground state properties of the systems and the variant self-consistent solution with accuracy inside the framework of DFT [108]. Plane waves are the precise Eigenfunctions of the homogeneous electron gas. Furthermore, the benefits of the plane-wave basis set are that they may be not biased to an atom, it is complete, there is a single convergence criterion and plane waves are mathematically easy and their derivatives are the product in k-space.

The Hellmann–Feynman theorem can be applied directly to calculate atomic forces because the plane wave does not depend on the position of the atoms [109]. The Coulomb potential of the electron-nucleus interaction is changed by using pseudopotential for the plane wave to be useful [110]. The basis set quality depends on a single parameter, the energy of a free electron,

$$E_c = \frac{\hbar^2(G+k)^2}{2m}, \quad (20)$$

where E_c is the cutoff energy. There are no wave function forces because of the independence of plane waves from an atomic role which means that the forces do not rely upon the basis set. Bloch's theorem simplifies the problem of calculating many plane waves for a countless range of k-points to a reduced variety of plane waves for a limitless quantity of k-points over the reciprocal lattice vectors. The plane-wave basis set has many advantages [111]:

- i. It is straightforward.
- ii. All necessary matrix elements can be efficaciously computed.
- iii. The basis doesn't prefer one place over some other, so there aren't any Pulay forces.
- iv. A single parameter controls the convergence of the basis.

Its disadvantage is that (i) the number of plane-waves needed is determined by the greatest curvature of the wavefunction and (ii) empty space has the same quality of representation and cost regions of interest [112].

3.4.3. Projector augmented wave

The projector augmented wave (PAW) is a technique used in ab initio electronic structure calculations to describe the bonding region to a high degree of accuracy while accounting for the large variations in the atom centre [113]. This approach is an electron method with easy to control approximations, elegant idea and it works with easy pseudo wave-functions that may be extended in a few plane waves. The primary idea of the PAW method is to divide the wave functions into two parts: a partial wave enlargement within an atom centered sphere, and an envelope function outside. Augmentation sphere is one

cut-off radius for every sort of atom, spheres ought not to overlap. PAW appears as a precise implementation of the DFT.

The method bridges the gap between the existing augmented wave techniques and the pseudopotential technique, underscoring the connection between these processes and combines their customs into a blended electronic structure method [114]. It is one of the principal goals of the PAW technique to introduce energy and potential impartial basis sets that had been as accurate and numerically efficient as the previously used augmented basis sets. The advantages of the PAW are [115]:

- i. No need to deal with inert core electrons.
- ii. Valence pseudo wave functions are smooth and without nodes inside the augmentation spheres.
- iii. Access to full all-electron wave functions and density.

3.5. Plane wave codes

3.5.1. CASTEP code

Cambridge Sequential Total Energy Package (CASTEP) is a leading code for calculating the electronic properties of materials from first principles using DFT with a plane-wave basis set [116]. It can simulate a wide variety of materials proprieties which include energetics, the structure at the atomic level, vibrational properties and electronic response properties. The simple quantity is the overall energy from which many other quantities are derived, aiming to calculate any physical property of the system. CASTEP can optimize the atomic geometry of a system in several exceptional ways [117].

Fast Fourier transforms (FFT) provide an efficient manner of transforming wave functions and potentials from real to reciprocal space and back, reduce reminiscence requirement and computational cost for operating with the Hamiltonian on the electronic wave functions. Furthermore, symmetry and constraints may be forced within the calculations, either as defined through the user, or automatically using in-built symmetry detection [86].

3.5.2. VASP code

Vienna Ab initio Simulation Package (VASP) [118] is a package for performing ab initio quantum mechanical molecular dynamics (MD) simulations using pseudopotentials or the PAW technique and a plane wave basis set [119]. It offers basic properties such as total energies, optimized geometries, trajectories, band shape and density of states plots, charge density. In addition, VASP is a quick and steady electronic structure method based on DFT [120].

VASP makes use of the PAW approach or ultra-soft pseudopotentials and includes a complete-featured symmetry code which determines the symmetry of arbitrary configurations automatically. The VASP carried out technique is based at the local density approximation with the free energy as a variational amount and an exact assessment of the immediately electronic ground state at each MD time step [121].

3.6. Molecular dynamics

Molecular dynamics (MD) simulation is a computational technique used to study the motions of atoms in a given system (e.g., a solid material or a solid solution could equally be liquids and gases) to understand and predict the structural, dynamic, kinetic, and /or equilibrium properties at a chosen conditions (e.g., compositions, temperatures, and pressures). MD is used to predict the stability, structural, dynamics, kinetic and

equilibrium properties [122]. MD is a powerful method for exploring the structure of solids, liquids and gases, and is also used for complicated system modelled at an atomic level. The purpose of MD simulation is to understand the properties of molecules in phases of their microscopic interaction and structure. The born-Oppenheimer approximation is used as an assumption that the nuclei are stationary [123]. Newton's second law of motion is applied to determine the acceleration of atoms:

$$F_i = m_i a_i$$

$$a_i = F_i / m_i, \quad (21)$$

where F is the force, m is the mass of the object and a is the acceleration. MD is characterized with the aid of a Force field which permits us to analyse the effect of temperature on a system. Advantages of molecular dynamics are:

- i. Gives a complete understanding of the system, everything can be calculated if all trajectories are recognized.
- ii. Easily accommodate non-equilibrium states and complicated simulation beyond thermal equilibrium.

Disadvantages of MD is that the complete knowledge of all trajectories is often much information than needed. MD methods are used in solid-state physics, with application in studies of ionic properties, modelling of phase transition and elucidating the structure and dynamical correlations. MD has kinetic energy that contributes to the total energy of the system. The simulations are historically achieved under situations of a regular number of particles (N), volume (V) and energy (E) (the constant NVE or microcanonical ensemble). But it can also be adapted to simulate from the canonical ensemble, and two other

common ensembles that are isothermal-isobaric (fixed NPT) and grand canonical (fixed μVT) [124].

To understand the properties of the chemical system in terms of their structure and microscopic interactions among various systems, MD simulations are employed. MD simulations produce information at the microscopic level, consisting of atomic positions and velocities [125]. In MD, atoms have interaction with each other. The forces appearing upon the atoms are originated by the interactions and the atoms circulate underneath the action of the instant force. The positions and forces change as the atoms move. In the current study, LAMMPS code within the MedeA [126] environment has been used to study the dynamics of the Ti-based shape memory alloys for binary, ternary and quaternary alloys.

3.6.1. LAMMPS Code

Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) [127] is a classical molecular dynamics simulation code designed to run efficaciously on parallel computers. It is designed to model atomic, polymeric, organic, metallic, granular and coarse-grained system employing various force fields and boundary conditions. Moreover, it may without difficulty be modified or extended with new competencies such as new force fields, atoms types and boundary conditions [128].

A function that makes LAMMPS appealing for materials modelling is that it allows the user to without problems adds functionality which includes a new potential, via well-described interfaces. The infrastructure offers neighbour lists of various kinds, permits the potential to be used in a hybrid simulation where two or more potentials are used to compute interaction between different groups of atoms. For a system of interacting particles,

LAMMPS capably calculate Newton's equation of motion and it is far found most efficient for a system whose particle fill a 3d rectangular box with more or less uniform density [129]. LAMMPS code is versatile, properly parallel overall performance, easy to increase and well documented.

The LAMMPS uses the powerful flowchart interface which enables the smooth setting up of the complicated calculations via connecting the stages. A stage may be a computation, e.g. energy minimization, NVT and NPT dynamics, as well as an operation along with putting the density to that computed via the previous stage or constructing a bigger simulation box. Any number of levels may be chained collectively to perform targeted, reproducible calculations [130]. In this study, we use the LAMMPS-EAM module which provides straight forward access to the embedded atom method (EAM) simulations in the MedeA environment [126].

CHAPTER 4

Ti-Based Binary Alloys (TiM, M=Pt, Ni, Co, Ta)

In this Chapter, the stability of cubic B2 Ti-based (TiPt, TiNi, TiCo and TiTa) binary alloys is investigated. The VASP code was employed to determine equilibrium lattice parameters, heats of formations, mechanical and electronic properties of the binary structures and the results are compared with the available experimental data where applicable. The phonon dispersions calculations are performed on the relaxed crystal structure and were evaluated using PHONON code [80] as embedded in Materials Design MedeA software package deal within VASP code.

4.1. Geometry optimization

4.1.1. Cutoff energy

In order to determine the appropriate cutoff energy for our structures (TiPt), single-point energy calculations were performed for different kinetic energy cutoffs at default number of k -points for each system within GGA-PBE. The method was employed owing to its robustness for metallic systems. We used ultrasoft pseudopotentials [131], which require significantly less computational resources than the norm-conserving potentials. In Figure 5 (a) we show the curves of total energy per atom against cutoff energy for TiPt structure. The energy cutoffs of 500 eV were chosen for TiPt structure since the energy gave a constant slope at that point and they yielded energy differences of less than 1 meV/atom.

4.1.2. k-points

In this section, we show the convergence of the total energies with respect to the k -point sampling set size, as illustrated in Figures 5 (b). We have carried out total energy calculation at fixed cutoff energy for TiPt structure while the number of k -points was varied. The total energy with respect to the number of k -points was considered converged when the energy change per atom (between two consecutive points) was within 1meV per atom. The k -points were chosen as 8x8x8 for TiPt structures, as shown in Figures 4 (b).

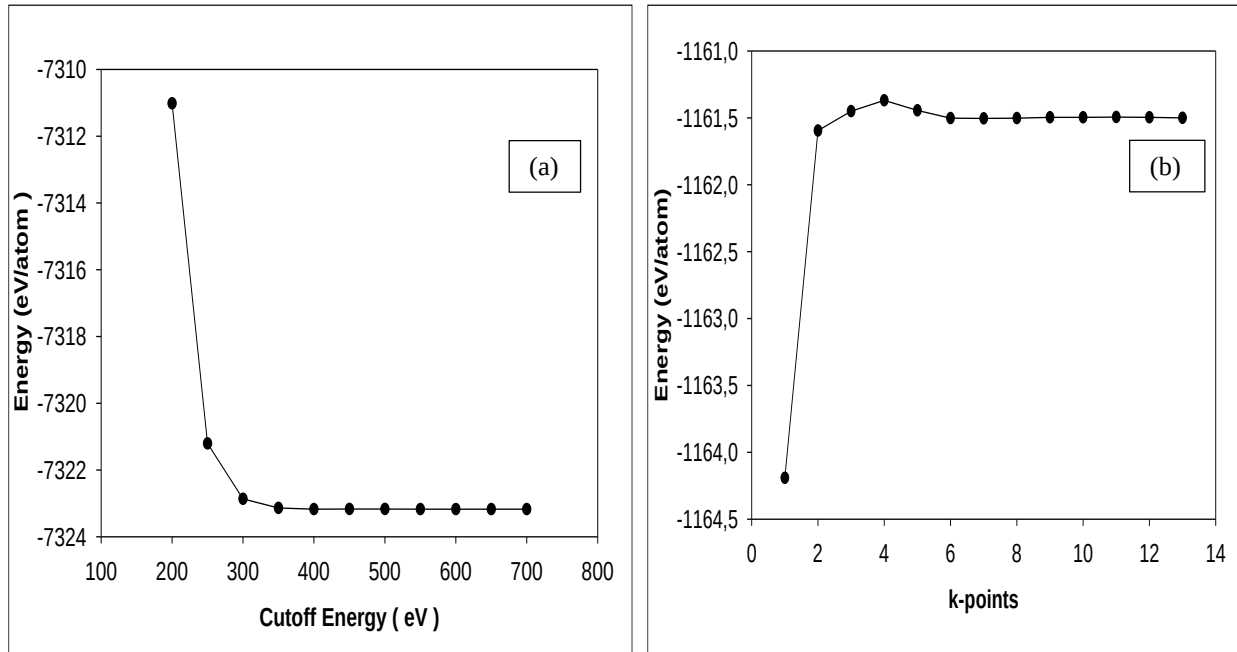


Figure 5. Graphs of (a) energy of formation vs. energy cutoff and (b) energy of formation vs. k-points for TiPt.

4.2. Structural and thermodynamic properties

In Table 1, the equilibrium lattice parameters and heats of formation for B2 TiM (M=Pt, Ni, Co, Ta) binary alloys are shown. The calculated equilibrium lattice parameter of B2 TiPt was observed to be 3.172 Å. In the previous studies, Donkersloot and van Vucht

reported the lattice parameter to be 3.192 Å [132], which is in good agreement with our current results to within 1 %. TiNi alloy (3.011 Å) show good agreement with experimental data to within 1 %. Moreover, the lattice parameter of TiCo was found to be 2.994 Å and is comparable to the available data to within 0.50 %. The lattice parameter of TiTa is 3.269 Å and it is about 3 % in agreement as compared to experimental findings results [133].

Now, to evaluate the thermodynamic stability of TiM systems, we calculated the heats of formation as discussed in Chapter 2 section 2.2.1. Note that the lowest value ($\Delta H_f < 0$) indicates the stability of the phase and the highest ($\Delta H_f > 0$) is associated with the instability of the material. The heats of formation of B2 TiPt structure is found to be more negative (-0.861 eV/atom) compared to other binary alloys suggesting that the structure is more energetically favourable. It is interesting to note that TiNi and TiCo are stable with the negative heats of formation value of about -0.403 and -0.527 eV/atom, respectively. The B2 TiTa phase is considered to be the least favourable since the structure occurs to have positive heats of formation (0.005 eV/atom), a value very close to zero.

Table 1. The equilibrium lattice parameters (Å) and heats of formation (eV/atom) of the B2 Ti-M binary alloys, with space group symmetry Pm-3m.

Structure	a	a	ΔH_f	ΔH_f
	<i>Calculated</i>	<i>Experimental</i>	<i>Calculated</i>	<i>Theoretical</i>
TiPt	3.179	3.192 [132, 134]	-0.861	-0.826 [135]
TiNi	3.011	3.030 [136]	-0.403	-0.640 [19]
TiCo	2.994	2.988 [137]	-0.527	
TiTa	3.269	3.350 [133]	0.005	

4.3. Elastic constants for Ti₅₀M₅₀ alloys

In Table 2, the calculated elastic constants (C_{ij} 's) and anisotropy (A) for the structures are shown. The accurate calculation of elasticity is critical in determining the mechanical stability and elastic properties of any given system. There are three (C_{11} , C_{12} , C_{44}) independent elastic constants for the cubic system as discussed in Chapter 2 Section 2.2.2. It is observed that TiPt fails to meet the cubic stability criterion, wherein C_{11} is found to be less than C_{12} ($C_{11} < C_{12}$) leading to a negative C' . This support the previous reports [3]. Interestingly, TiNi obeys the mechanical stability criterion with all the C_{ij} 's being positive in agreement with the previous studies [138]. The binary TiCo and TiTa are also mechanically stable satisfying the cubic stability condition. The predicted C_{ij} 's for the systems are in reasonable agreement with available experimental data.

Anisotropy factor (A) is a measure of the degree of anisotropy in materials. It takes the value of 1 for an isotropic material [139]. The calculated anisotropy gave a value of 2.52 (TiNi) in good agreement with the experimental findings ($A = 2.40$) [138]. TiNi and TiCo are elastically anisotropic materials since the anisotropy factor A is larger than 1. There is a stronger correlation between C_{44} and shear modulus C' of TiTa (since the values are

closer to each other) and thus the structure is considered as isotropic material since the anisotropic factor approaches unity ($A \approx 1$) [18]. These findings are consistent with the experimental findings [138, 140].

Table 2. The elastic constants, anisotropy, Bulk, Shear and Young's moduli for Ti-M alloys.

Structure	TiPt		TiNi		TiCo		TiTa
	<i>Calculated</i>	<i>Theoretical</i>	<i>Calculated</i>	<i>Experimental</i>	<i>Calculated</i>	<i>Experimental</i>	<i>Calculated</i>
C₁₁	145	130 [21]	190	162 [138]	267	203 [140]	204
C₁₂	210	270	144	132	216	129	121
C₄₄	45	58	58	36	44	68	40
C' ((C ₁₁ - C ₁₂)/2)	-32	-70	23	15	26	37	42
A (C ₄₄ /C')			2.52	2.40	1.72	1.83	0.95
B	183		158	155 [141]	178	143	149
G	80		28	25	52	54	40
E	186		79	71	142	154	111
B/G	2.28		5.57		3.42		3.70

In order to investigate the ductility, hardness and stiffness, we determined the shear (G), bulk (B) and Young's moduli of binary Ti-based alloys and the results are shown in Table 2. TiPt is observed to have the highest bulk modulus of 183 GPa as compared to other systems, indicating that it has a strong resistance to volume change under applied pressure. TiCo with the bulk modulus of 178 GPa is the second hardest followed by TiNi. However, TiTa has the least bulk modulus (149 GPa) as compared to other binary systems which show that it has weak resistance to volume change.

Recall that shear modulus (G) is concerned with the rigidity of the material where the large value of G indicates that the material is highly rigid otherwise flexible. The value of G of TiPt is larger indicating that the material is highly rigid as compared to TiNi, TiCo and TiTa alloys. Moreover, TiNi occurs to have a smaller value of shear modulus ($G = 28$ GPa) which indicate that the alloy is less rigid.

Young's moduli (E) is a measure of solids stiffness, where the low value of E suggests that the material is elastic while the high value of E suggests inelastic material. Note that E was calculated as shown in Table 2. It is seen that TiPt have the highest Young's moduli of 186 GPa, it is considered to be inelastic (high stiffness), followed by TiCo and TiTa. TiNi has the lowest value ($E = 79$ GPa) which suggests the material is less stiff.

The ratio B/G known as Pugh's ratio is a simple relationship related to brittle and ductile behaviour of materials. A high B/G ratio is associated with ductility, whereas a low value corresponds to the brittleness [142]. The critical value separating ductile and brittle material is 1.75. In this work, the obtained results indicate that TiPt, TiCo, TiNi and TiTa compounds can be classified as ductile materials since the B/G ratio is greater than the critical value ($B/G > 1.75$). Moreover, TiNi structure occurs to be more ductile with the highest B/G value of 5.57, whereas TiPt is found to be the least ductile structure ($B/G = 2.28$) as compared to other alloys under study.

4.4. Phonon dispersion curves for $Ti_{50}M_{50}$ alloys

In Figures 6 to 9, the phonon dispersions of binary TiPt, TiNi, TiCo and TiTa alloys are presented. The phonon dispersions of the structures are used to investigate the vibrational stability of these alloys. The presence of soft modes or negative frequency

phonon branches suggests the instability of the materials while the absence of phonon modes in the negative frequency suggest vibrational stability [3]. In Figure 6, there are soft modes observed along the high symmetry direction which confirms that TiPt is vibrationally unstable. This confirms the elastic instability of TiPt predicted by elastic constants. This suggests that the presence of soft modes are attributed to the negative value of shear modulus C' . This analysis is in agreement with the previous report [3]. The phonon DOS show that the soft modes observed were due to the high vibration of Pt at approximately -3 THz. It is well-known that B2 TiPt is a high temperature structure which is unstable at low temperature, as reflected from the binary TiPt phase diagram [52].

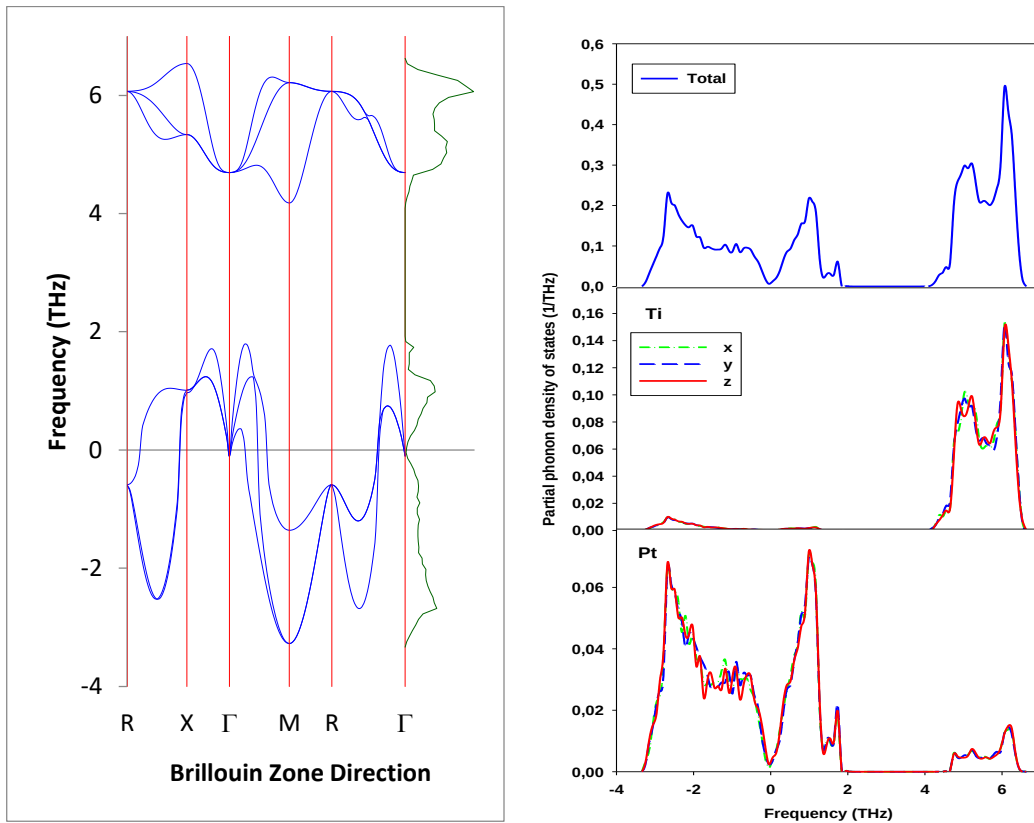


Figure 6. The phonon dispersion curves for B2 Ti₅₀Pt₅₀ binary alloys. The partial DOS show contribution of Ti and Pt.

Figure 7 shows the phonon dispersion curves for TiNi binary alloy. The dispersion spectrum exhibit two sets of phonon modes namely the optical and acoustic modes separating the upper and lower sets within the diagram. The optical modes of the phonon dispersion curve mainly due to the contribution of Ti atoms whereas the acoustic emanates from the Ni atoms as depicted by their phonon DOS. It was observed that TiNi is vibrationally unstable because there are soft modes observed in the negative frequency. The observed soft modes are along with the high symmetry directions, M, R-X and R- Γ . Our calculation confirms the existence of phonon instabilities in B2 phases of TiNi, in agreement with previous experimental and theoretical studies [20].

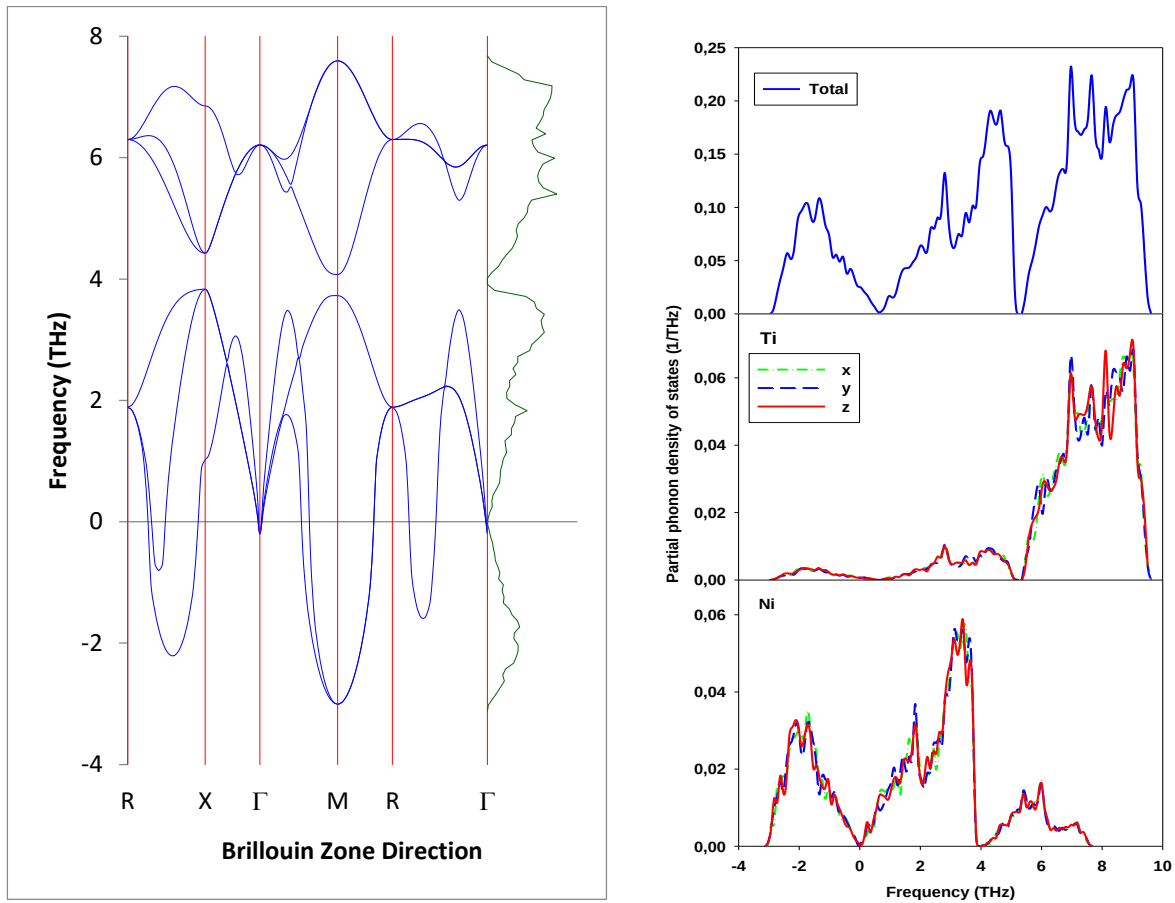


Figure 7. The phonon dispersion curves for B2 Ti₅₀Ni₅₀ binary alloys. The partial DOS show contribution of Ti and Ni.

In Figure 8, the phonon dispersion curve of TiCo is shown to investigate the vibrational stability at 50:50 concentration. It is noticed that TiCo occurs to be vibrationally stable due to the absence of soft modes in the negative frequency. Phonon DOS show that Co is dominant at approximately 4 THz whereas Ti at about 7 THz. These results are in good agreement with the calculated elastic constants discussed above. Previous investigations reported that TiCo is a stable phase at low temperatures because of its low martensitic transformation temperatures [21].

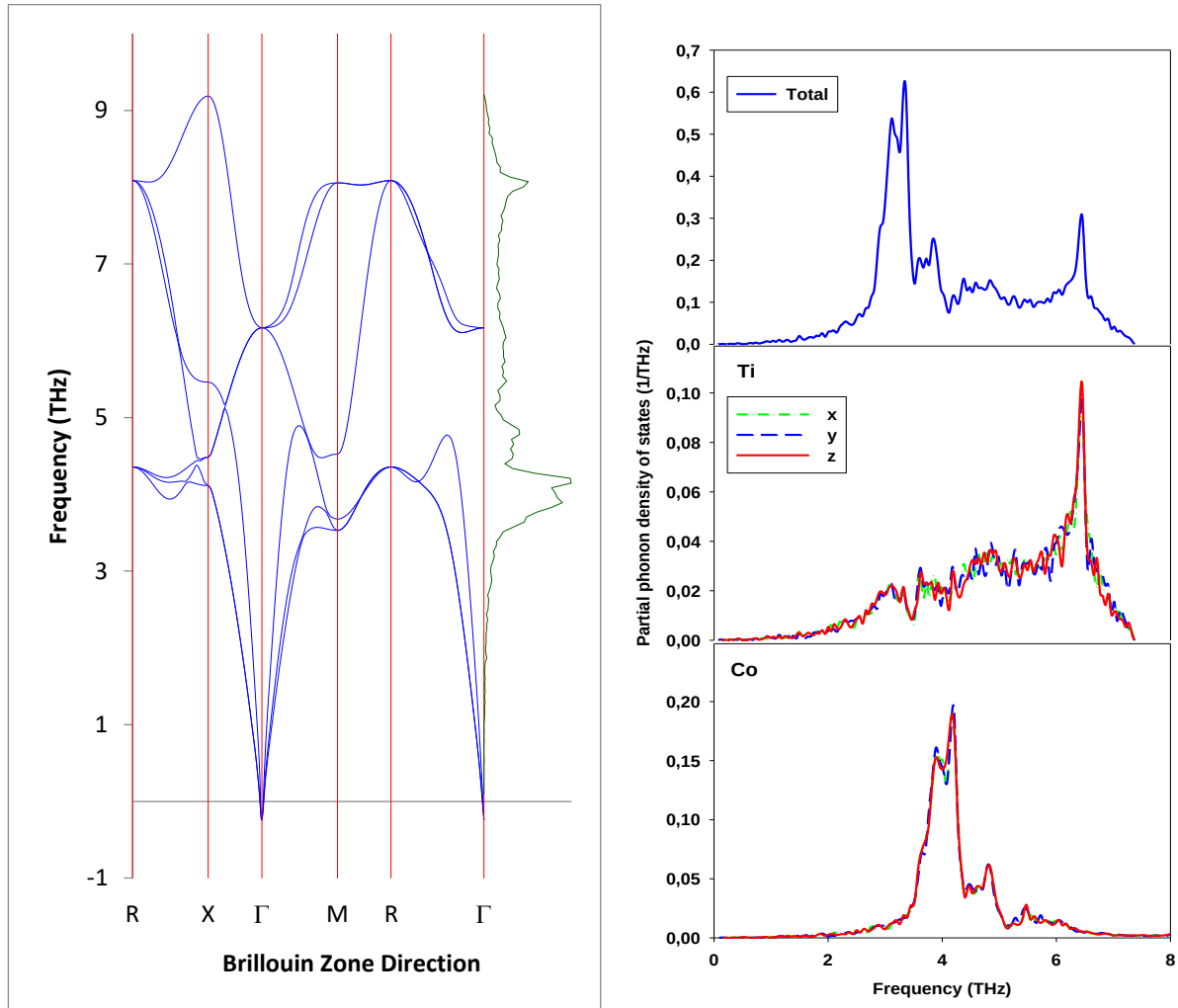


Figure 8. The phonon dispersion curves for B2 Ti₅₀Co₅₀ binary alloys. The partial DOS show contribution of Ti and Co.

Phonon dispersion curves and phonon density of states for the TiTa was calculated and is shown in Figure 9. The phonon dispersion curve is characterized by soft modes along R-X, M and R- Γ high symmetry directions similar to that of TiNi. These soft modes emanate mostly from the vibration of Ta atoms. Clearly, the soft modes are observed at approximately -3.5 THz along the M, R-X and R- Γ high symmetry directions. The presence of soft mode is associated with vibrational instability of the system. The phonon DOS show that there is a vibration of Ta and Ti in the negative frequency which suggest that the material is vibrationally unstable.

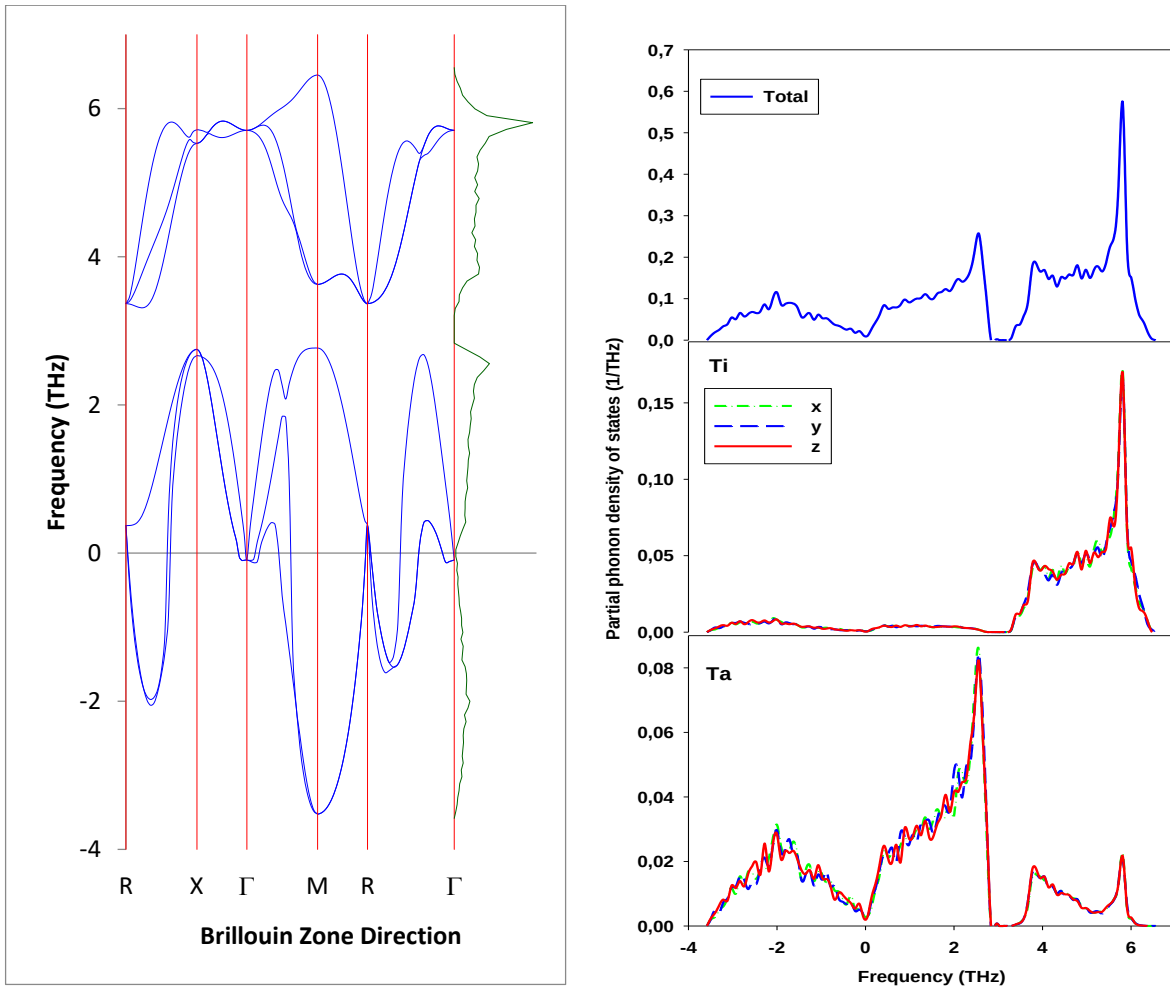


Figure 9. The phonon dispersion curves for B2 Ti₅₀Ta₅₀ binary alloys. The partial DOS show contribution of Ti and Ta.

4.5. Electronic density of states for $\text{Ti}_{50}\text{M}_{50}$ alloys

In order to better examine the differences in electronic structures of different alloys, it is important to analyse the behaviour of the total density of states (DOS) and partial density of states (PDOS). DOS of a system describes the number of states at every stage that is available to be occupied by electrons. Note that higher stability corresponds to lower total DOS value at the Fermi level whereas less stability is associated with high DOS value of the structures [21].

The total and PDOS of B2 TiPt alloys have been calculated and are shown in Figures 10. The DOS curves consist of two sets of peaks separated by pseudogap near the Fermi level ($E-E_f = 0$). Lower energy peaks are mainly occupied by Pt d-states whereas the higher energy peaks are predominantly from the Ti d-states. TiPt B2 structures (Figure 10) are relatively less stable since the Fermi level (E_f) hit the DOS at the edge of the peak and the pseudogap is observed in the valence band. This is due to the high contribution of Ti d-states at the Fermi level, as suggested by partial DOS. Moreover, there is a less contribution of Pt at the Fermi level. These analyses are in good agreement with the theoretical results reported by John et al [41].

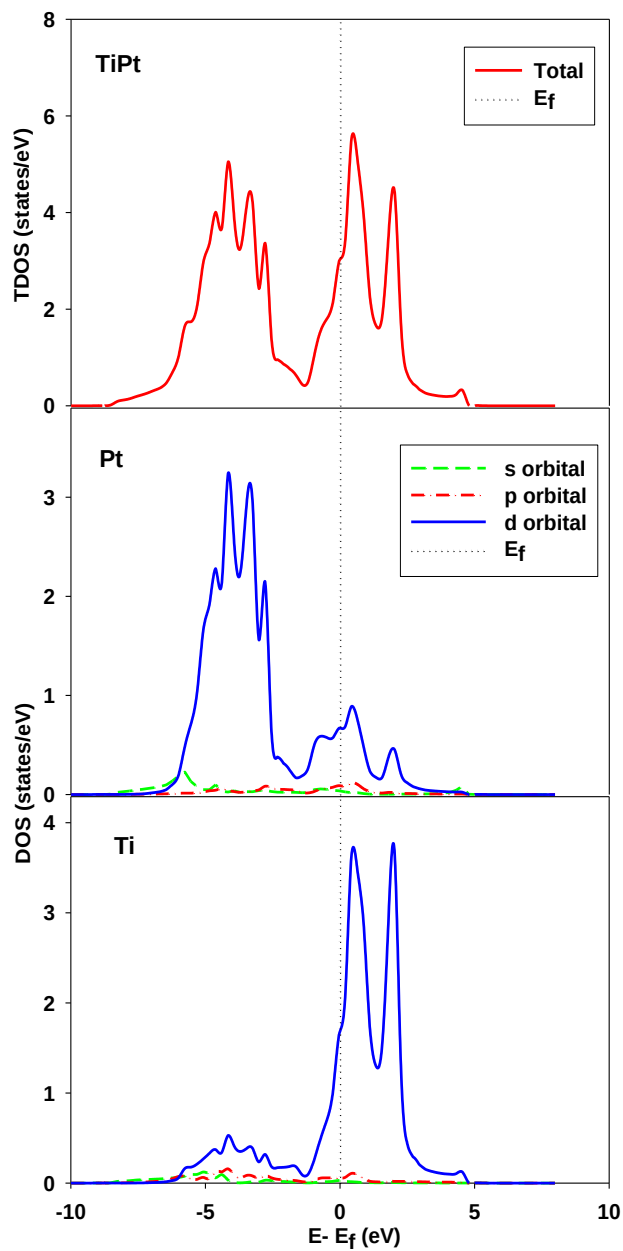


Figure 10. Total and partial density of states for Ti₅₀Pt₅₀ alloy. The Fermi energy is taken at energy zero ($E - E_f = 0$).

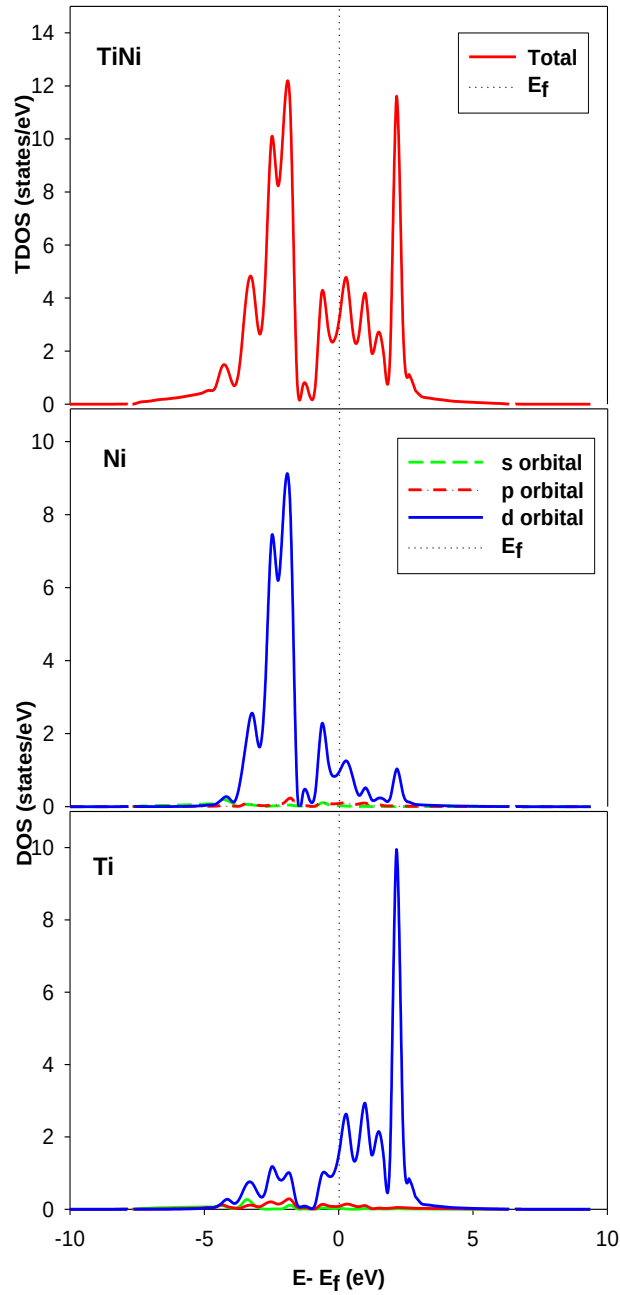


Figure 11. Total and partial density of states for $\text{Ti}_{50}\text{Ni}_{50}$ alloy. The Fermi energy is taken at energy zero ($E - E_f = 0$).

Figure 11 shows the total DOS and PDOS of TiNi alloys at 50:50 concentration. Lower energy peaks are occupied by sets of Ni d-states while high energy peaks are characterized by Ti d-states. Ni d-states are dominant at approximately -3 eV and negligible contribution of Ti is observed at this energy. The pseudogap lies between two

small peaks at the Fermi level. The peak at the E_f emanates from contributions of both Ni and Ti d-states with the latter being slightly dominant. Ni d-states small peak to the left of E_f whereas Ti d-states to the right of E_f . High stats at E_f correspond to a less stable structure.

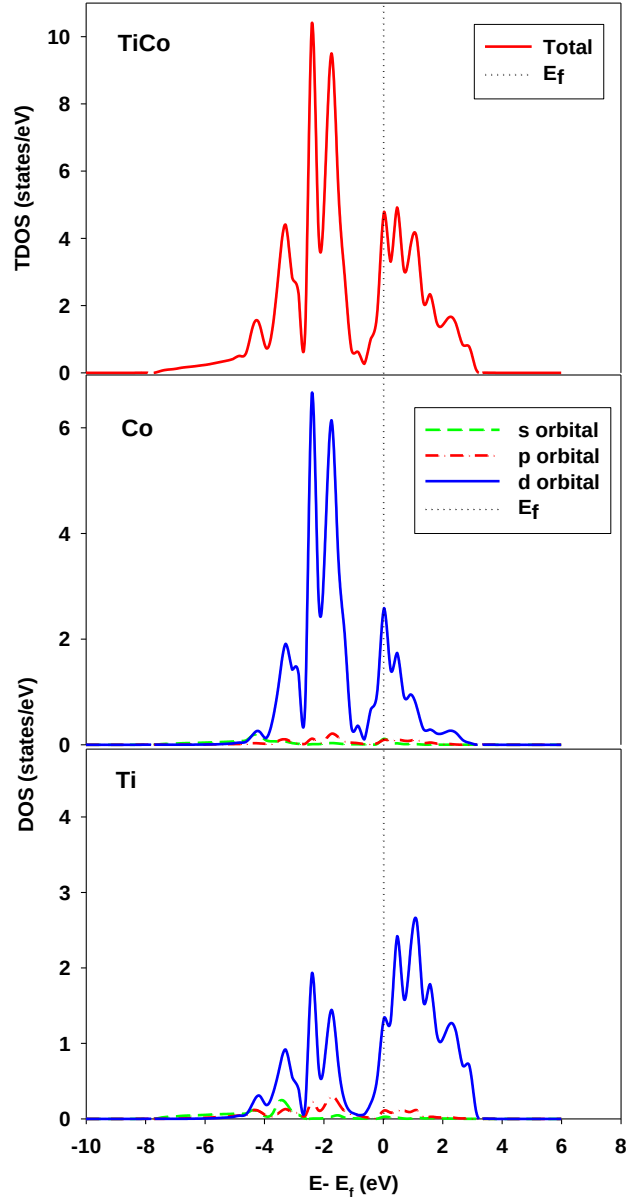


Figure 12. Total and partial density of states for $\text{Ti}_{50}\text{Co}_{50}$ alloy. The Fermi energy is taken at energy zero ($E - E_f = 0$).

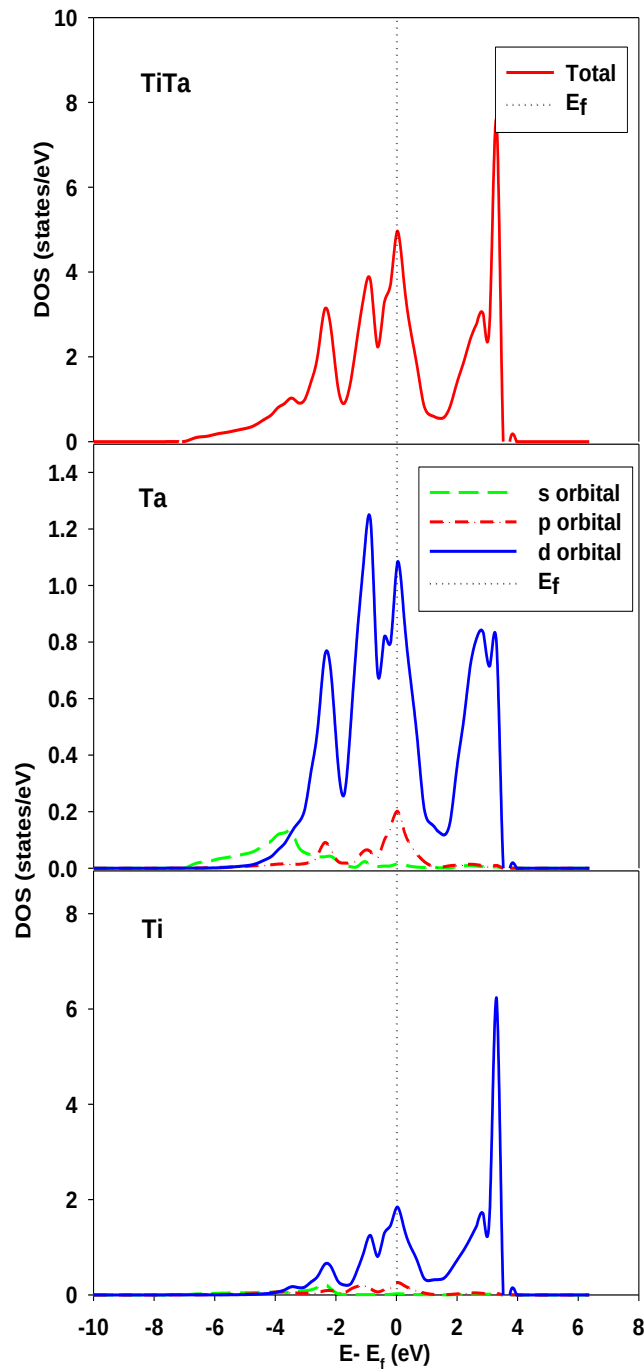


Figure 13. Total and partial density of states for $\text{Ti}_{50}\text{Ta}_{50}$ alloy. The Fermi energy is taken at energy zero ($E - E_f = 0$).

The total and PDOS of the B2 TiCo structures are shown in Figure 12. The Fermi level for the TiCo hits the top of DOS peak confirming less stability of the system. Co d-states are dominant at approximately -2 eV and less contribution of Ti towards the valence band.

The peak at E_f emanates from the high contribution of the Co d-states and less of Ti d-states. Figure 13 shows the total and PDOS of B2 TiTa systems. It is interesting to observe that the E_f hits the DOS curve at the peak for TiTa. The pseudogap is observed at the right of E_f in the conduction band. It is noted that there is a high contribution of Ti d-states (approximately 1.8 states/eV) at the Fermi level. Ta d-states are dominant at the energy of approximately -3 eV. Moreover, there is a contribution of Ti in the conduction band at approximately 3 eV.

4.6. Summary

In this chapter, we presented DFT results on the binary B2 phase alloys which are TiPt, TiNi, TiCo and TiTa structures. The equilibrium lattice parameters of the TiPt, TiNi, TiCo and TiTa have been calculated and were observed to be in good agreement with the experimental findings to within 5 %. Moreover, B2 TiPt was found to be the most stable alloy as suggested by the low heats of formation value in agreement with previous studies. It was observed that binary TiTa is thermodynamically unstable due to high heats of formation value ($\Delta H_f > 0$).

Elastic properties of TiNi, TiCo and TiTa suggest that the systems are mechanically stable due to positive C_{ij} 's values. However, TiPt was found to be mechanically unstable because of negative shear modulus (C') in agreement with previous theoretical and experimental findings. It was further indicated that B2 TiPt is an excessive temperature material and is unstable at low temperatures. According to the phonon dispersion curves, TiCo was found to be vibrationally stable due to the absence of soft modes, whereas TiPt, TiNi and TiTa had been observed to be vibrationally unstable due to the presence of soft modes along the high symmetry directions. There is a good correlation between the

predicted elastic constant and phonon dispersion curve for TiPt and TiCo whereas for TiNi and TiTa showed the difference.

The electronic stability was deduced by observing the behaviour of DOS and PDOS with respect to E_f and the pseudogap. We observed that TiCo and TiTa binary alloys are characterized by the peak at the Fermi level whereas TiNi and TiPt Fermi level hit the DOS at the shoulder of arising peak. These findings suggest that TiPt and TiNi are more favourable which is in good agreement with the predicted heats of formation.

CHAPTER 5

Ti₅₀Pt_{50-x}M_x (M=V, Ta, Hf) TERNARY ALLOYS

In this chapter, the effect of ternary alloying on the cubic TiPt is investigated. In Chapter 4, TiPt was found to be the most thermodynamically stable structure in comparison to different binary alloys due to its low heats of formation. However, it is mechanically unstable because of negative shear modulus ($C' < 0$). The experimental findings showed that TiPt has negligible recovery strain [17] as discussed in Chapter 2. Thus ternary alloys had been recommended to improve the recovery strain and the mechanical properties of the alloy [3, 17] thus by addition of the third element.

The VASP code was used to perform the ternary alloy calculations, all systems were constructed using the B2 structure with a 2x2x2 supercell consisting of sixteen atoms. The substitutional search tool was used to find possible composition by replacing Pt with V, Ta and Hf atoms on B2 TiPt ($x = 6.25, 18.75$ and 25). Their equilibrium lattice parameter, heats of formation, elastic properties, phonon dispersions and density of states have been determined.

5.1. Equilibrium lattice parameter and heats of formation

In Table 3, the calculated lattice parameters and heats of formation of the Ti₅₀Pt_{50-x}M_x (M=Ta, V, Hf) at different concentrations ($x = 6.25, 18.75, 25$) are shown. The calculated results show that the equilibrium lattice parameter for Ti₅₀Pt_{50-x}V_x decreases minimally as we increase the concentration in the system. It was found that the partial substitution of Pt with Ta and Hf increase the lattice parameters of the Ti₅₀Pt_{50-x}Ta_x and Ti₅₀Pt_{50-x}Hf_x,

respectively. This implies that the structure becomes larger in volume. This may be due to the difference in atomic radius, that is the atomic radius of Ta (220 pm) and Hf (225 pm) is bigger than that of Ti (215 pm) and Pt (175 pm) atoms. The lattice parameters acquired for the ternary alloys are in good agreement or comparable to lattice parameter by Bozollo et al [143] particular at 5 at.% Ta (3.166), V (3.144) and Hf (3.169). Mahlangu et al reported that as Co content is increased in the system, the lattice parameter decreases minimally [53].

Table 3. Equilibrium lattice parameters (a) and Heats of formation (ΔH_f) of $\text{Ti}_{50}\text{Pt}_{50-x}\text{M}_x$ (M= V, Ta, Hf, Co) alloys.

structure	a (Å)	ΔH_f (eV/atom)
$\text{Ti}_{50}\text{Pt}_{43.75}\text{V}_{6.25}$	3.156	-0.84
$\text{Ti}_{50}\text{Pt}_{31.25}\text{V}_{18.75}$	3.123	-0.71
$\text{Ti}_{50}\text{Pt}_{25}\text{V}_{25}$	3.121	-0.63
$\text{Ti}_{50}\text{Pt}_{43.75}\text{Ta}_{6.25}$	3.174	-0.85
$\text{Ti}_{50}\text{Pt}_{31.25}\text{Ta}_{18.25}$	3.175	-0.64
$\text{Ti}_{50}\text{Pt}_{25}\text{Ta}_{25}$	3.195	-0.60
$\text{Ti}_{50}\text{Pt}_{43.75}\text{Hf}_{6.25}$	3.191	-0.82
$\text{Ti}_{50}\text{Pt}_{31.25}\text{Hf}_{18.75}$	3.217	-0.54
$\text{Ti}_{50}\text{Pt}_{25}\text{Hf}_{25}$	3.254	-0.50
$\text{Ti}_{50}\text{Pt}_{43.75}\text{Co}_{6.25}$ [53]	3.149	-0.74
$\text{Ti}_{50}\text{Pt}_{31.25}\text{Co}_{18.75}$	3.104	-0.61
$\text{Ti}_{50}\text{Pt}_{25}\text{Co}_{25}$	3.073	-0.58

In Table 3, we also show the heats of formation (ΔH_f) for V, Ta and Hf additions. Recall that the lowest ΔH_f ($\Delta H_f < 0$) indicate that the material is stable while the highest value ($\Delta H_f > 0$) suggest less stability of materials as discussed in Section 2.2.1. Thus, the calculated ΔH_f of the structures suggests that as the V, Ta and Hf content is increased,

ΔH_f becomes less negative suggesting reduced stability of the B2 $\text{Ti}_{50}\text{Pt}_{50}$ system. The 25 at.% M ($\text{Ti}_{50}\text{Pt}_{25}\text{V}_{25}$, $\text{Ti}_{50}\text{Pt}_{25}\text{Ta}_{25}$ and $\text{Ti}_{50}\text{Pt}_{25}\text{Hf}_{25}$) have been determined to be the least stable due to their reduced ΔH_f value with -0.63, -0.60 and -0.50 eV/atom for V, Ta and Hf, respectively. This may suggest that these ternary alloys prefer lower concentration substitution since the systems are thermodynamically more stable at low content of V, Ta and Hf (6.25 at.%). Previously, Bozollo et al [143] found a similar trend of the heats of formation at 5 at.% addition which is reasonably well with our current findings. The predicted ΔH_f values are in agreement with those reported for 5 at.% V, Ta, Hf which are -0.73, -0.65 and -0.68 eV/atoms [143], respectively. It was reported that ΔH_f increases with an increase in the Co content which suggest that B2 TiPt becomes less stable [53].

5.2. Elastic constants for $\text{Ti}_{50}\text{Pt}_{50-x}\text{M}_x$ alloys

In Table 4, the calculated elastic properties, bulk, shear and Young's modulus for the B2 $\text{Ti}_{50}\text{Pt}_{50-x}\text{M}_x$ (M = Ta, V, Hf) are shown. It is interesting to note that all the independent elastic constants C_{11} , C_{12} and C_{44} are positive for all composition which includes the V, Ta and Hf content. It is noted that when 6.25 at.% of dopant (V, Ta and Hf) is added, the C_{11} becomes greater than C_{12} resulting in a positive shear modulus C' ($C' > 0$) suggesting the mechanical stability of the phase according to the stability criterion for cubic crystal [3].

A similar trend is observed for 18.75 and 25 at.% additions on the $\text{Ti}_{50}\text{Pt}_{50}$ with all the C_{ij} 's being positive. It can be deduced that addition of Ta, V and Hf reduce the martensitic transformation temperature of binary TiPt due to an increase in the shear moduli ($C' > 0$) in comparison to that of the TiPt ($C' = -32$ GPa) [3]. This observation is similar to previous studies. It was reported that the addition of 6.25 at.% V reduces the martensitic

transformation temperature of $\text{Ti}_{50}\text{Pt}_{50}$ from $M_s = 1247$ K to $M_s = 1162$ K [56]. Previous studies show that $\text{Ti}_{50}\text{Pt}_{50-x}\text{Co}_x$ (6.25, 18.75, 25 at.%) is mechanically stable suggested by elastic constants satisfying the cubic stability criteria [53].

We have also calculated the A of the ternary systems to determine anisotropic behaviour in Table 4. Recall that the origin of B19' phase is a result of the coupling among C_{44} and C' [21]. The calculated A of 6.25, 18.75 and 25 at.% of V and Ta is smaller as compared to that of Hf at.%. Interestingly, the anisotropy A decreases as we increase Hf concentration in the B2 TiPt system. The C' at $x = 6.25$ is rather smaller (7) in comparison to the 18.75 and 25 at.% concentrations, resulting in a larger A . $\text{Ti}_{50}\text{Pt}_{43.75}\text{Hf}_{6.25}$ has higher A value of 7.48 which indicate that the material is anisotropic.

Table 4. Elastic properties (GPa) of $\text{Ti}_{50}\text{Pt}_{50-x}\text{M}_x$ ($M = \text{V}, \text{Ta}, \text{Hf}$) ternaries and their anisotropy A .

structure	C_{11}	C_{12}	C_{44}	C'	A
$\text{Ti}_{50}\text{Pt}_{50}$	145	210	45	-32	
$\text{Ti}_{50}\text{Pt}_{43.75}\text{V}_{6.25}$	231	167	49	32	1.52
$\text{Ti}_{50}\text{Pt}_{31.25}\text{V}_{18.75}$	304	120	48	92	0.52
$\text{Ti}_{50}\text{Pt}_{25}\text{V}_{25}$	255	131	78	62	1.26
$\text{Ti}_{50}\text{Pt}_{43.75}\text{Ta}_{6.25}$	243	162	51	40	1.27
$\text{Ti}_{50}\text{Pt}_{31.25}\text{Ta}_{18.25}$	282	131	29	76	0.39
$\text{Ti}_{50}\text{Pt}_{25}\text{Ta}_{25}$	286	131	66	79	0.83
$\text{Ti}_{50}\text{Pt}_{43.75}\text{Hf}_{6.25}$	189	175	53	7	7.48
$\text{Ti}_{50}\text{Pt}_{31.25}\text{Hf}_{18.75}$	197	151	53	23	2.26
$\text{Ti}_{50}\text{Pt}_{25}\text{Hf}_{25}$	196	124	67	36	1.87

In order to investigate the ductility, hardness and plasticity of the ternary systems, we have calculated the shear (G), bulk (B), Young's (E) moduli and Pugh's ratio (B/G) of $\text{Ti}_{50}\text{Pt}_{50-x}\text{M}_x$ (M = V, Ta, Hf) as shown in Table 5. The Bulk moduli are used to deduce the hardness of these alloys, where a high bulk moduli indicate that the structures are resistant to compression. $\text{Ti}_{50}\text{Pt}_{43.75}\text{V}_{6.25}$, $\text{Ti}_{50}\text{Pt}_{43.75}\text{Ta}_{6.25}$, and $\text{Ti}_{50}\text{Pt}_{43.75}\text{Hf}_{6.25}$ have a strong resistance to volume change due to its high bulk moduli. We note that as the content of V, Ta and Hf increases, the value of bulk modulus decreases. It can be deduced that at 6.25 at.% V, Ta and Hf composition, the structures are less rigid since they have low shear moduli. However, when the content of V, Ta and Hf are decreased, the Bulk moduli also decreases the ternary alloys becomes less rigid. Furthermore, the calculated results show that Young's modulus is low at 6.25 at.% V and Hf, and 18.75 at.% Ta which suggest that they are less stiff. The obtained results indicate that $\text{Ti}_{50}\text{Pt}_{50-x}\text{V}_x$, $\text{Ti}_{50}\text{Pt}_{50-x}\text{Ta}_x$ and $\text{Ti}_{50}\text{Pt}_{50-x}\text{Hf}_x$ ternary alloys are classified as ductile materials since B/G is greater than the critical value at all concentrations.

Table 5. Bulk (B), Shear (G), Young (E) modulus, and Pugh's ratio (B/G) of $\text{Ti}_{50}\text{Pt}_{50-x}\text{M}_x$ (M=V, Ta, Hf) ternary alloys.

structure	B (GPa)	G(GPa)	E(GPa)	B/G
$\text{Ti}_{50}\text{Pt}_{43.75}\text{V}_{6.25}$	188	42	117	4.51
$\text{Ti}_{50}\text{Pt}_{31.25}\text{V}_{18.75}$	181	62	168	2.91
$\text{Ti}_{50}\text{Pt}_{25}\text{V}_{25}$	172	71	188	2.41
$\text{Ti}_{50}\text{Pt}_{43.75}\text{Ta}_{6.25}$	189	47	129	4.07
$\text{Ti}_{50}\text{Pt}_{31.25}\text{Ta}_{18.25}$	182	43	120	4.21
$\text{Ti}_{50}\text{Pt}_{25}\text{Ta}_{25}$	182	71	187	2.60
$\text{Ti}_{50}\text{Pt}_{43.75}\text{Hf}_{6.25}$	180	25	70	7.34
$\text{Ti}_{50}\text{Pt}_{31.25}\text{Hf}_{18.75}$	167	38	105	4.44
$\text{Ti}_{50}\text{Pt}_{25}\text{Hf}_{25}$	148	52	140	2.82

5.3. Phonon dispersion curves for $\text{Ti}_{50}\text{Pt}_{50-x}\text{M}_x$ alloys

In Figures 14 to 16, phonon dispersion curves and phonon density of states for the $\text{Ti}_{50}\text{Pt}_{50-x}\text{Ta}_x$ ($x = 6.25, 18.75$ and 25) are presented. Previously, the phonon dispersion curves of the binary B2 $\text{Ti}_{50}\text{Pt}_{50}$ phase was reported in which the phonon spectra were mostly characterised by the soft modes. These soft modes are attributed to the negative value of shear modulus C' ($C' = -32$ GPa). In this section, we analyse the effect of ternary alloying on the B2 structures to observe how the dopant influence the appearance of soft modes. The $2 \times 2 \times 2$ supercell is used to determine the phonon dispersion curves and phonon DOS for the ternaries.

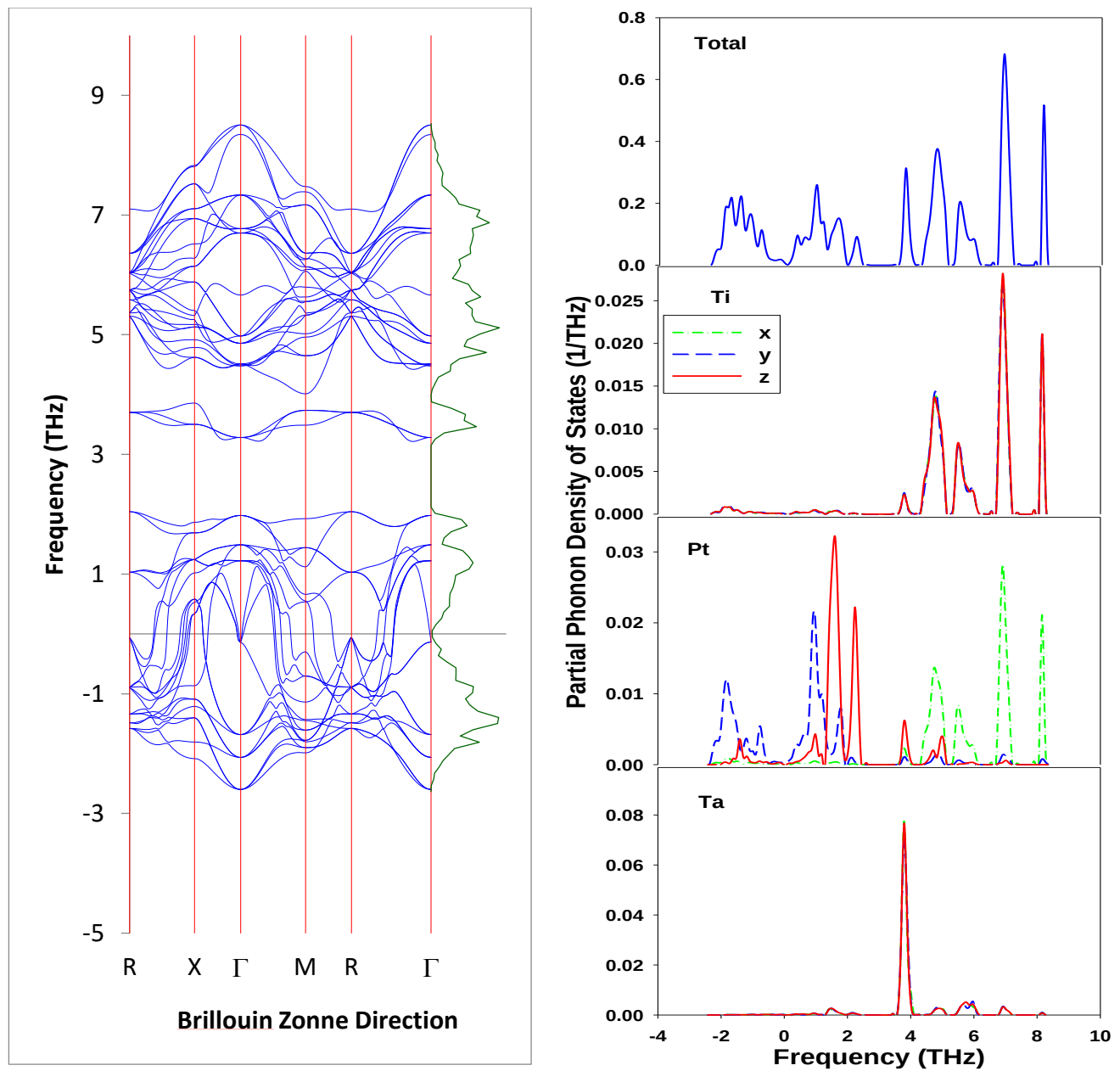


Figure 14. Phonon dispersion curves and partial phonon DOS of the $\text{Ti}_{50}\text{Pt}_{43.75}\text{Ta}_{6.25}$.

Now, in Figure 14 we show the phonon dispersion and phonon density of state for $\text{Ti}_{50}\text{Pt}_{43.75}\text{Ta}_{6.25}$. It is seen that the $\text{Ti}_{50}\text{Pt}_{50-x}\text{Ta}_x$ alloy is unstable at $x = 6.25$ additions. This observation is attributed to vibrations in the negative frequency displayed by the phonon dispersion curves. The soft modes observed along high symmetry directions are due to the high vibration of Pt atoms in the system as suggested by the phonon DOS. These

vibrations are observed along the Pt y-axis in the negative frequency at approximately -2 THz.

Figure 15 show the phonon dispersion and phonon DOS for $\text{Ti}_{50}\text{Pt}_{31.25}\text{Ta}_{18.75}$. It is noted that as the concentration is increased to $x = 18.75$ at. % Ta, there are no vibrations observed in the negative frequency indicating the stability at these compositions. These findings agree with the predicted elastic constants displaying the stability of TiPtTa at low temperature. Moreover, phonon dispersion and phonon DOS suggest that addition of 25 at.% Ta stabilizes TiPt as shown in Figure 16. There are no vibrations in the negative frequency displayed by the phonon dispersion curves which suggest that $\text{Ti}_{50}\text{Pt}_{25}\text{Ta}_{25}$ is stable. These results suggest that Ta addition at 18.75 at.% and above stabilizes the B2 $\text{Ti}_{50}\text{Pt}_{50}$ alloys.

Phonon dispersion curves and phonon density of states for the $\text{Ti}_{50}\text{Pt}_{50-x}\text{V}_x$ ($x = 6.25, 18.75$ and 25) have been calculated as shown in Figures 17, 18 and 19, respectively. In Figure 17, the optical modes of the phonon dispersion curves are contributed to Ti atoms whereas the acoustic emanates from the Pt and V atoms as depicted by their phonon DOS respectively. $\text{Ti}_{50}\text{Pt}_{43.75}\text{V}_{6.25}$ is unstable displaying soft modes along with the high symmetry directions as shown in Figure 17. These soft modes have the lowest frequency at approximately -2 THz mainly due to the Pt contributions. These soft modes observed emanates mainly from the Pt z-axis directions. Figure 18 shows the phonon dispersion and phonon DOS for $\text{Ti}_{50}\text{Pt}_{31.25}\text{V}_{18.75}$. There are no vibrations observed in the negative direction which suggest that the material is stable. As the V addition increases to 25 at.%, the system is stable as shown in Figure 19. The addition of 18.75 and 25 at.% V stabilizes the B2 TiPt alloy.

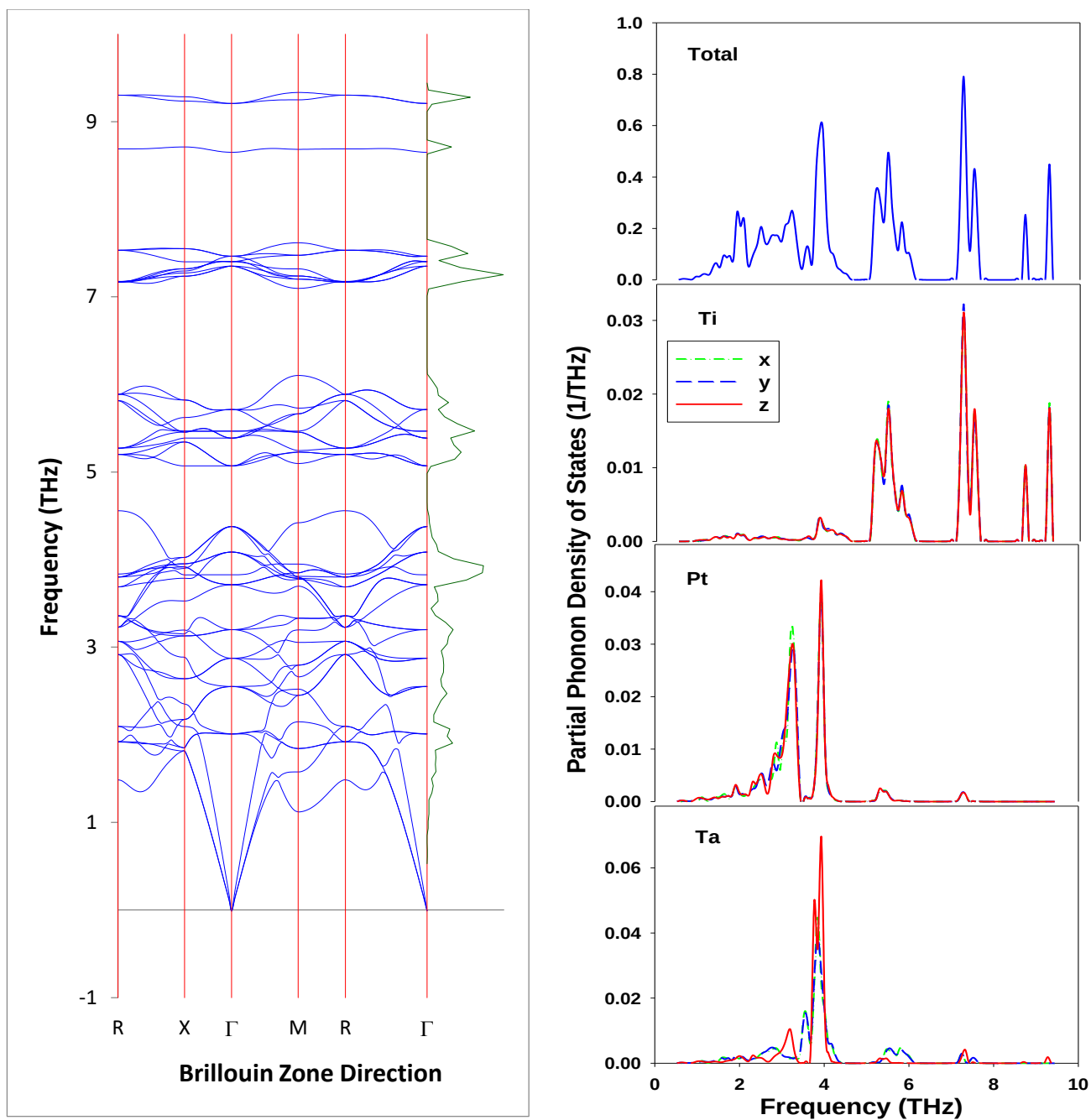


Figure 15. Phonon dispersion curves and partial phonon DOS of the $\text{Ti}_{50}\text{Pt}_{31.25}\text{Ta}_{18.75}$.

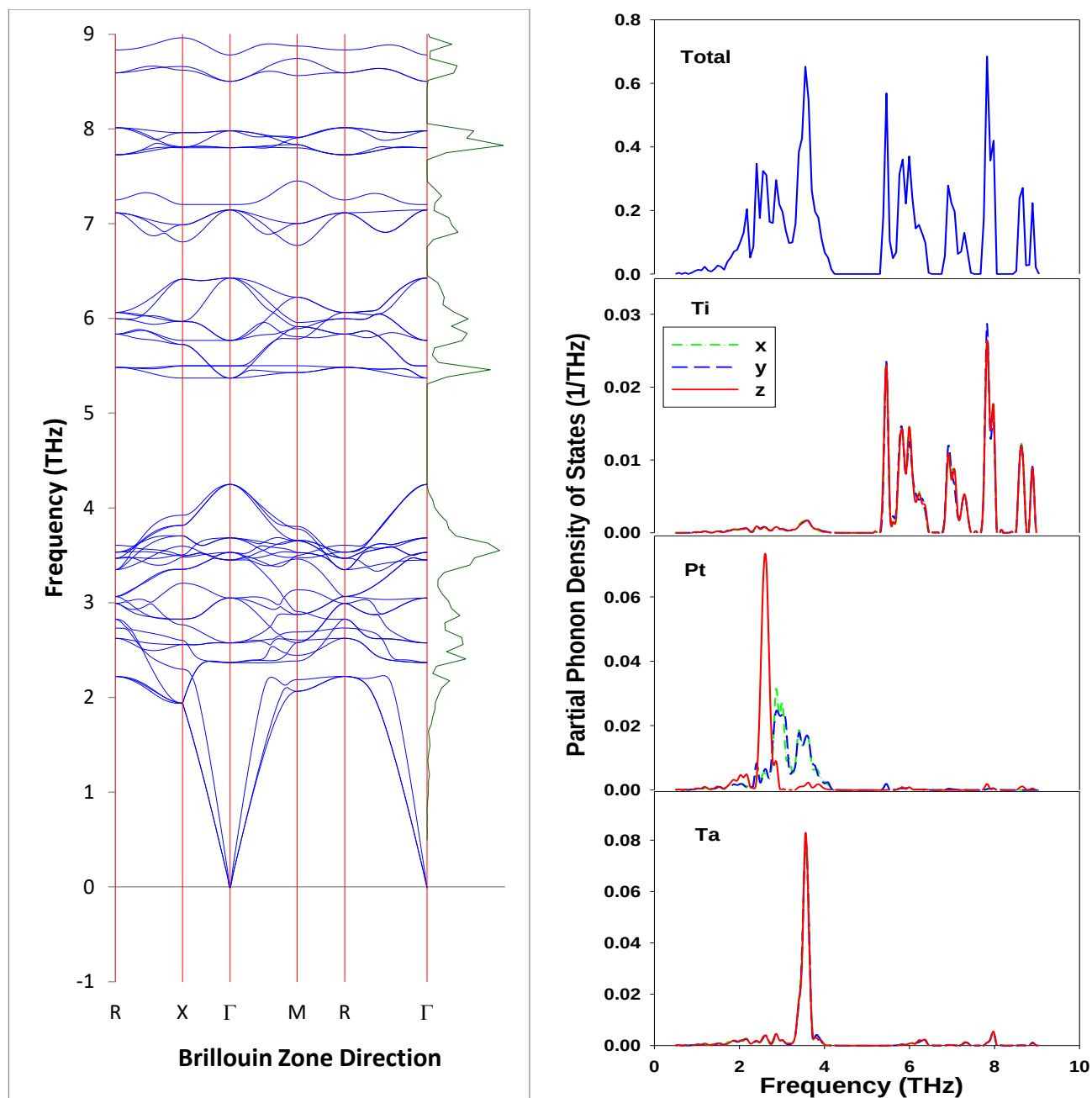


Figure 16. Phonon dispersion curves and partial phonon DOS of the $\text{Ti}_{50}\text{Pt}_{25}\text{Ta}_{25}$.

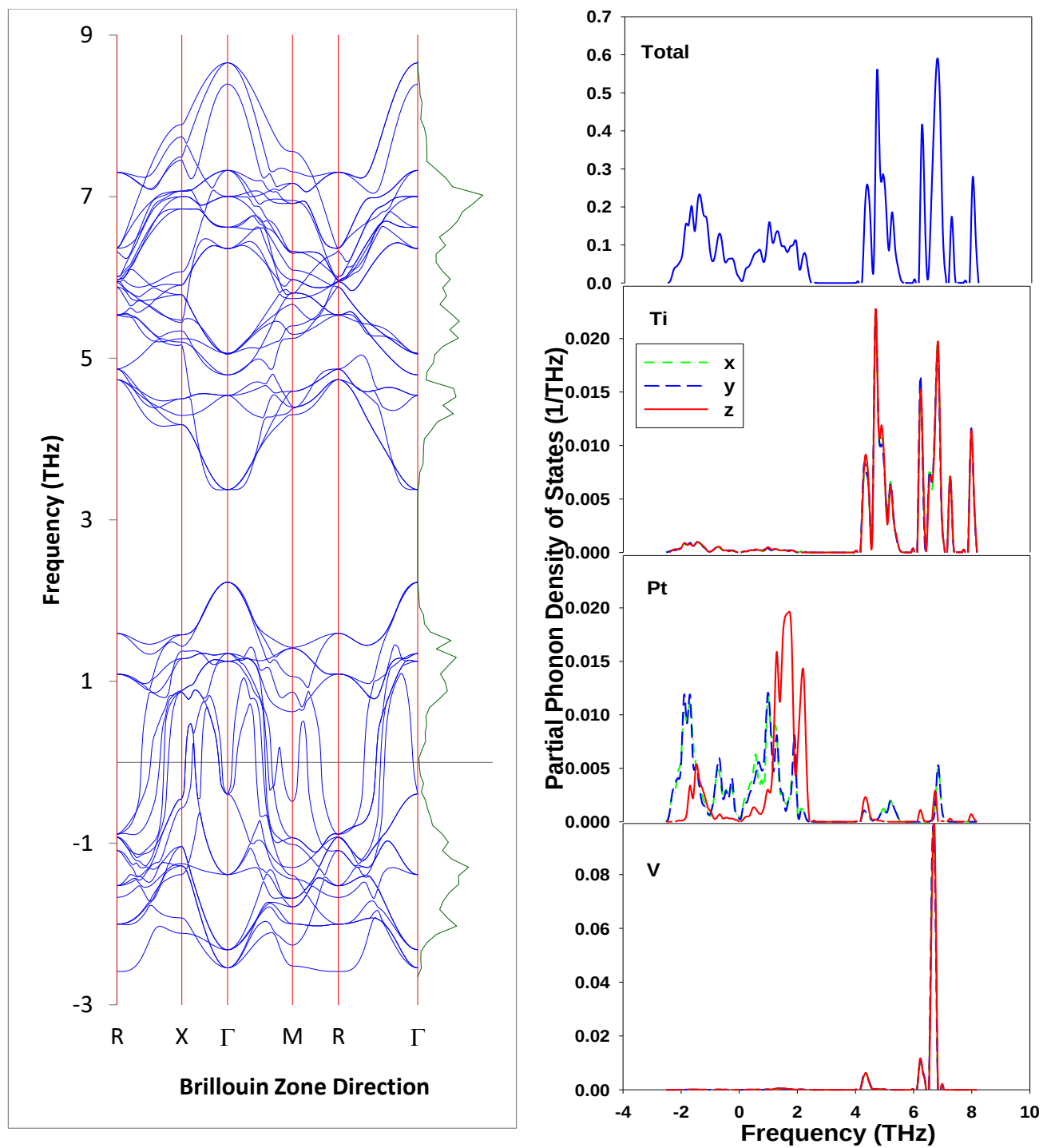


Figure 17. Phonon dispersion curves and partial phonon DOS of the $\text{Ti}_{50}\text{Pt}_{43.75}\text{V}_{6.25}$.

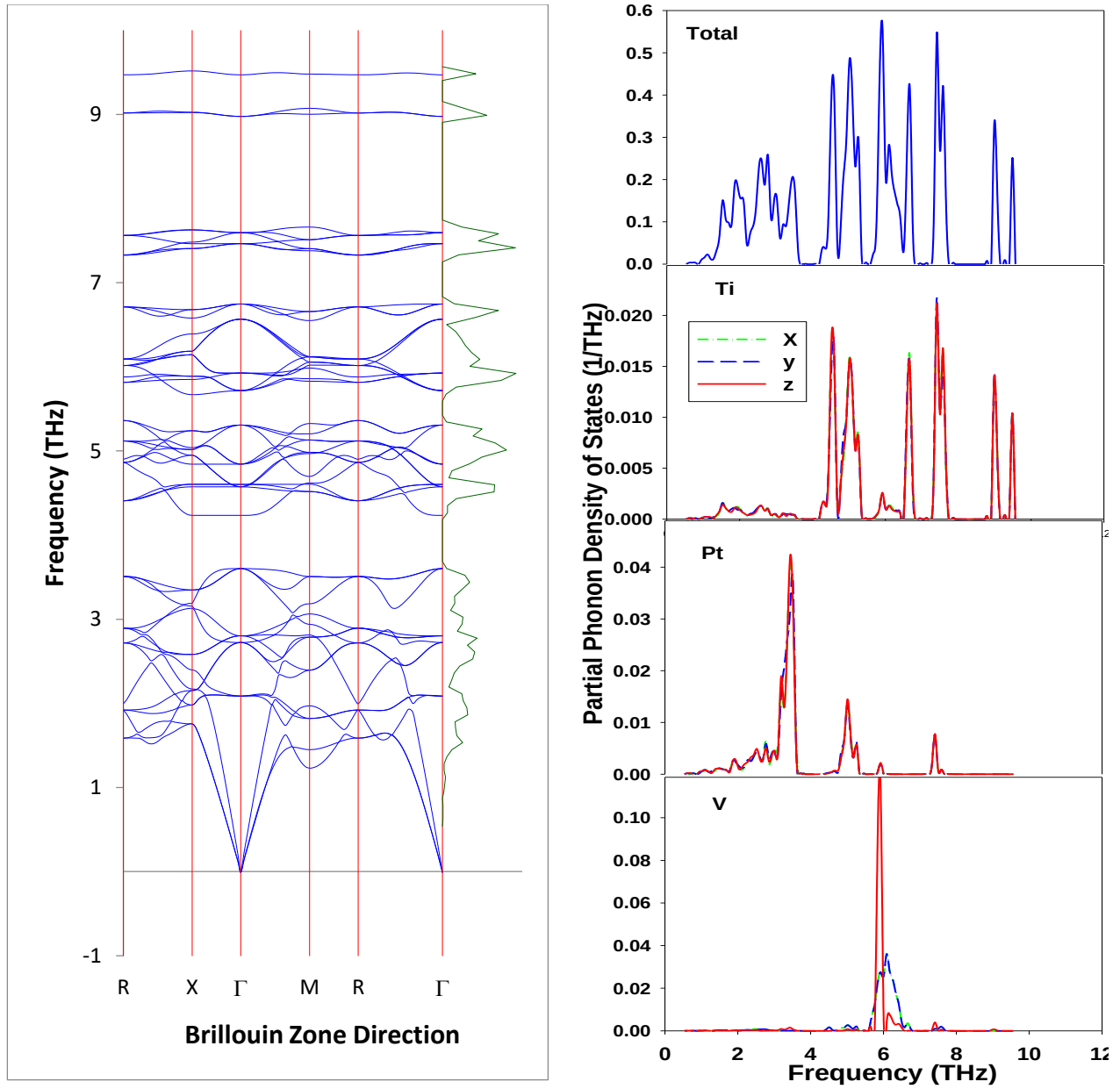


Figure 18. Phonon dispersion curves and partial phonon DOS of the $\text{Ti}_{50}\text{Pt}_{31.25}\text{V}_{18.75}$.

Interestingly, as the content vanadium increases, the systems become vibrationally stable with no soft modes observed at the phonon curves in the negative frequency. These findings suggest that V content material greater than or equal to 18.75 vibrationally stabilises the B2 TiPt phase in agreement with the elastic constants wherein the values

of A for 18.75 and 25 at. % is barely smaller compared with the $\text{Ti}_{50}\text{Pt}_{43.75}\text{V}_{6.25}$ structure. These results suggest that the addition of V stabilises the B2 TiPt alloys.

Phonon dispersion calculations had been performed to investigate the vibrational properties of $\text{Ti}_{50}\text{Pt}_{50-x}\text{Hf}_x$ ternary alloys at different concentration and are shown in Figures 20, 21 and 22. These curves show an interesting behaviour as Hf concentration increases in the system. $\text{Ti}_{50}\text{Pt}_{43.75}\text{Hf}_{6.25}$ is unstable due to observed vibrations in the negative frequency along with the high symmetry directions, displayed by way of phonon dispersion curves. The observed soft modes are due to the excessive vibration of Pt atoms in the negative direction.

It is interesting to observe that at higher content of hafnium ($x = 18.75$ and 25), the material becomes vibrationally stable with no soft modes observed at the phonon curves in the negative frequency. For $x = 18.75$, the vibrations above 4 THz emanates mostly from the Ti and Hf z-axis direction at the same time as under 4 THz are in most cases from the Pt and Hf y and z-axis directions. Moreover, at $x = 25$ the phonon DOS shows that vibrations below 4 THz are due to Pt and Hf whilst those above 4 THz are contributions from Ti atoms for different concentration of Hf.

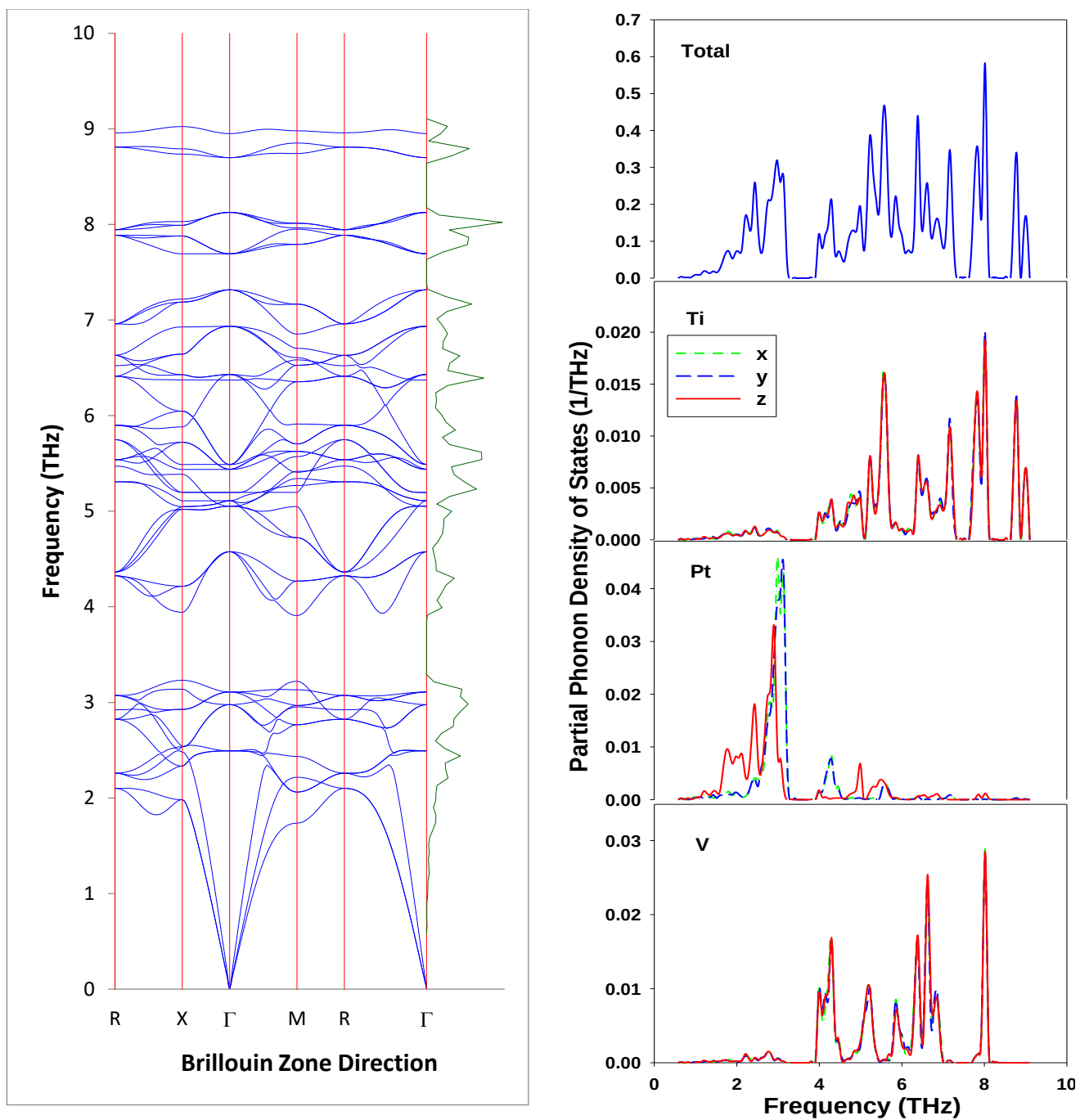


Figure 19. Phonon dispersion curves and partial phonon DOS of the $\text{Ti}_{50}\text{Pt}_{25}\text{V}_{25}$.

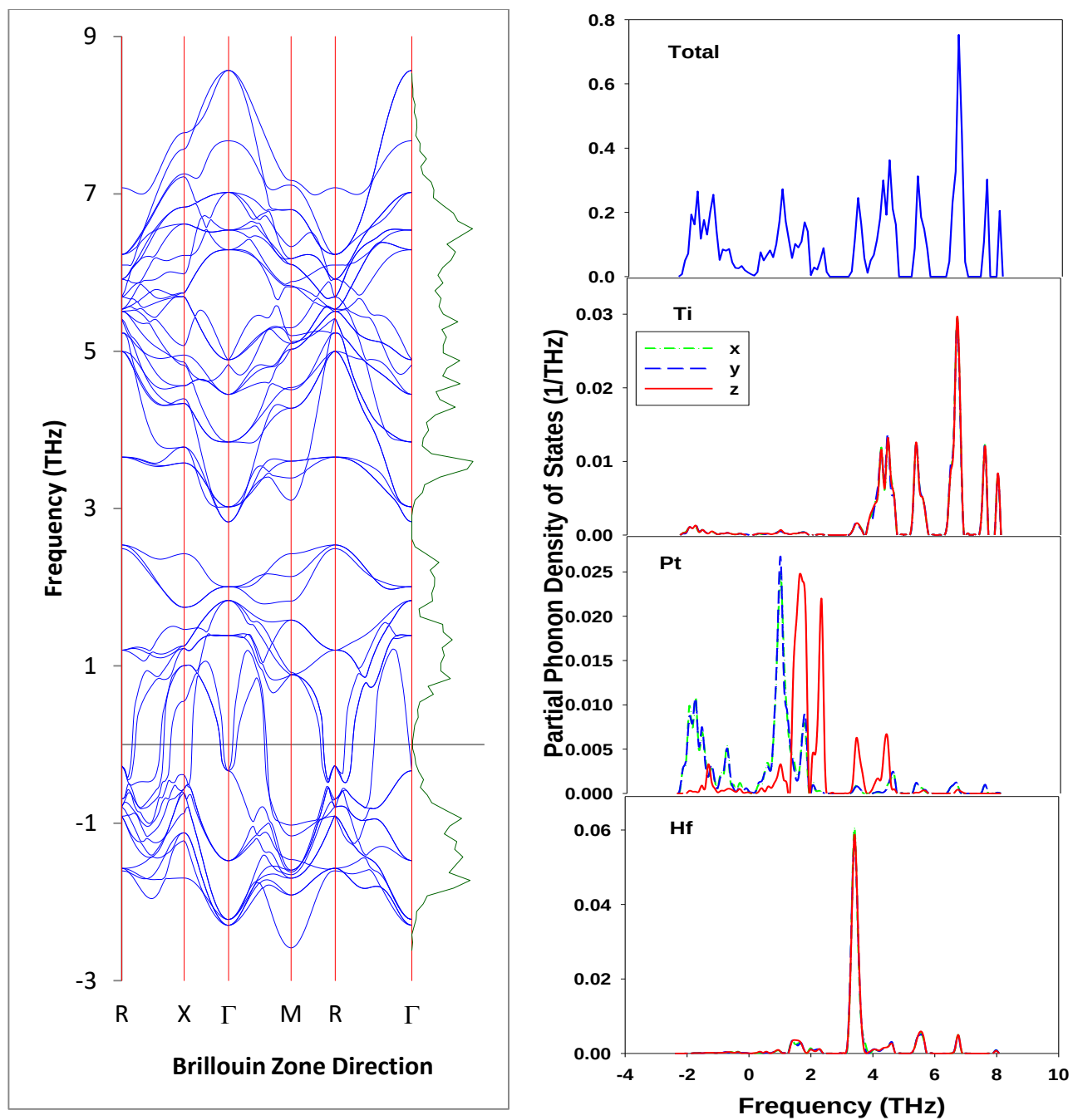


Figure 20. Phonon dispersion curves and partial phonon DOS of the $\text{Ti}_{50}\text{Pt}_{43.75}\text{Hf}_{6.25}$.

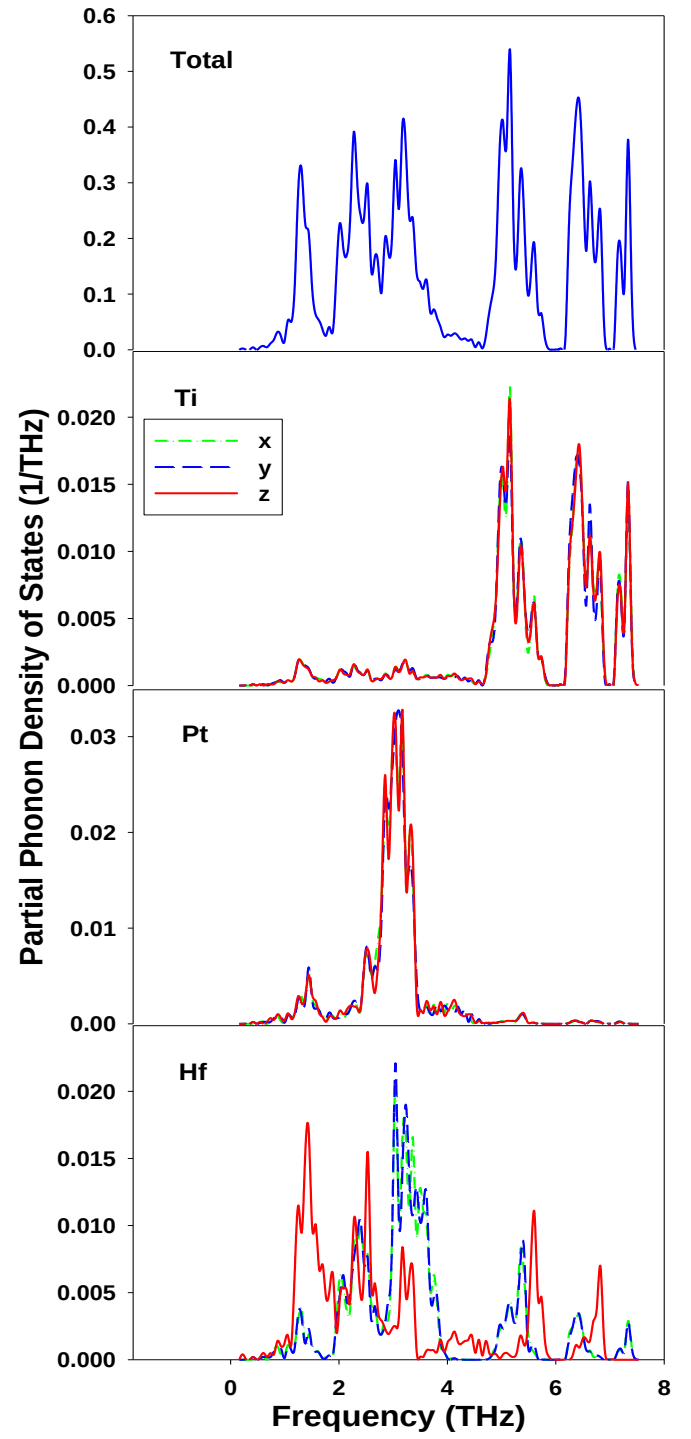
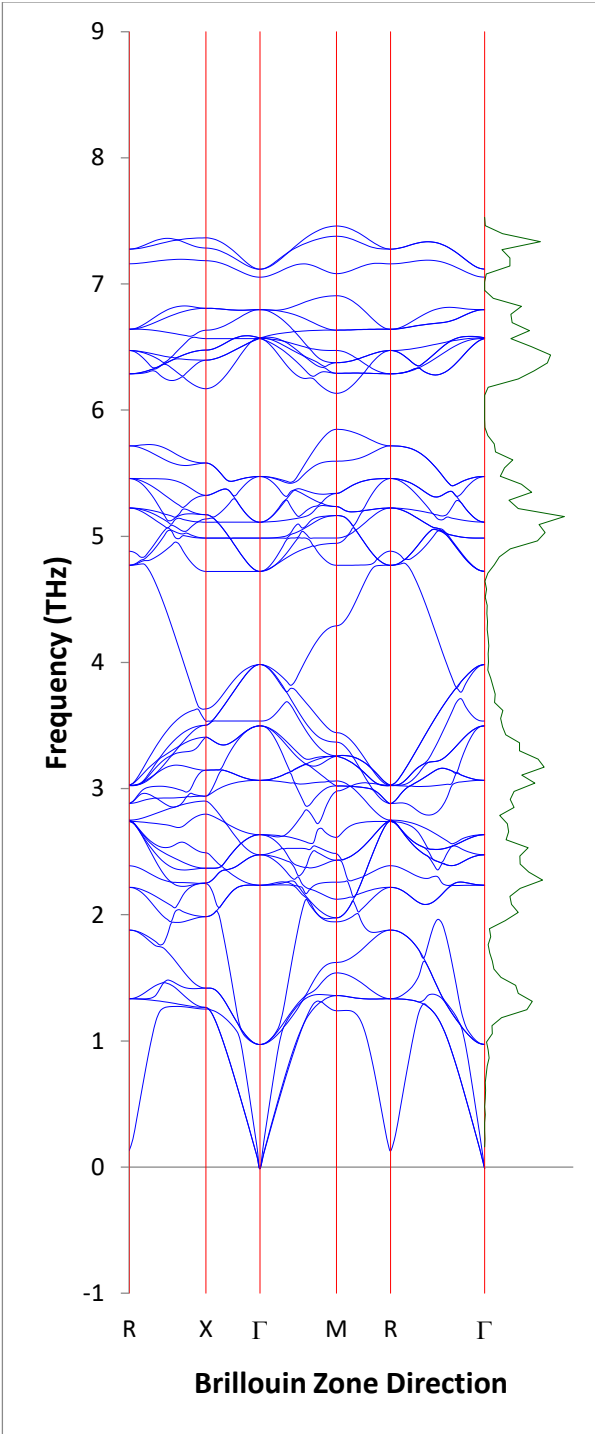


Figure 21. Phonon dispersion curves and partial phonon DOS of the $\text{Ti}_{50}\text{Pt}_{31.25}\text{Hf}_{18.75}$.

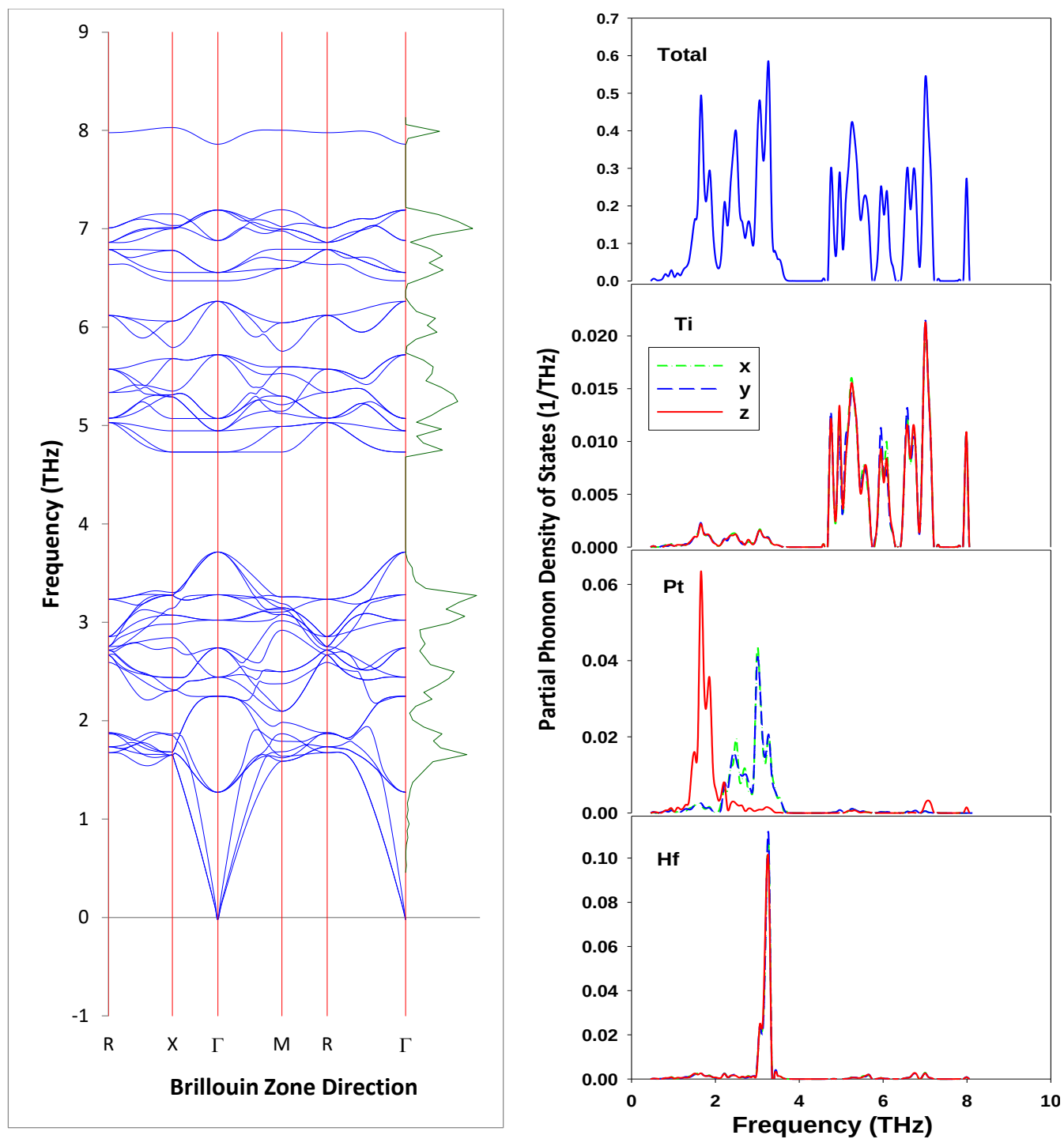


Figure 22. Phonon dispersion curves and partial phonon DOS of the $\text{Ti}_{50}\text{Pt}_{25}\text{Hf}_{25}$.

5.4. Density of states for $\text{Ti}_{50}\text{Pt}_{50-x}\text{M}_x$ alloys

The total and partial density of states (PDOS) of B2 $\text{Ti}_{50}\text{Pt}_{50-x}\text{V}_x$, $\text{Ti}_{50}\text{Pt}_{50-x}\text{Hf}_x$ and $\text{Ti}_{50}\text{Pt}_{50-x}\text{Ta}_x$ were calculated to investigate their relationship between electronic structure and stability. Previously, Figure 10 shows that $\text{Ti}_{50}\text{Pt}_{50}$ is unstable since the E_f is characterized by a peak suggested by the DOS. The total DOS and the PDOS of the B2 $\text{Ti}_{50}\text{Pt}_{50-x}\text{V}_x$ structures at different composition are presented in Figures 23 and 24. In Figure 23 (a), at about -4.5 eV, we observe a dominant peak which is ascribed a contribution of mainly Pt d states and less of Ti and V d-states. A peak at about -1 eV is predominate of V d-states, with less contribution from Pt and Ti d-states. Moreover, we observe a peak at the Fermi level ($E-E_f = 0$) which is a contribution of Ti d-states, which suggest that Ti influences the stability of the material. However, another peak is observed at about 2 eV which is predominate of V d-states contribution.

Figure 23 (b) shows the total and partial DOS for $\text{Ti}_{50}\text{Pt}_{31.25}\text{V}_{18.75}$. Further addition up to 18.75 at.% V, we notice a shift of peak in the valence band at about -4.5 (Figure 23 (a)) to -5 eV. We observe a peak at -1 eV which contribution of V and Ti d-states with a negligible contribution of Pt d-states. Moreover, the E_f coincides with a small peak which is the contribution of V and Ti d-states.

In Figure 24, the total and partial DOS for $\text{Ti}_{50}\text{Pt}_{25}\text{V}_{25}$ are presented. The dominant peak observed at about -4 eV is attributed to Pt and Ti d-states with a negligible contribution of V orbitals. There is a new peak observed at about -3 eV which is contribution mainly from Pt d-states and less of Ti d-states. We observe a small peak at the Fermi level which contribution of Ti and V d-states. Moreover, Pt d-states have no influence in the conduction band, only Ti and V d-states contribute towards the conduction band.

Furthermore, at 25 at.% V, the structure becomes more unfavourable since DOS shift towards the valence band, this is in support with the predicted heats of formation.

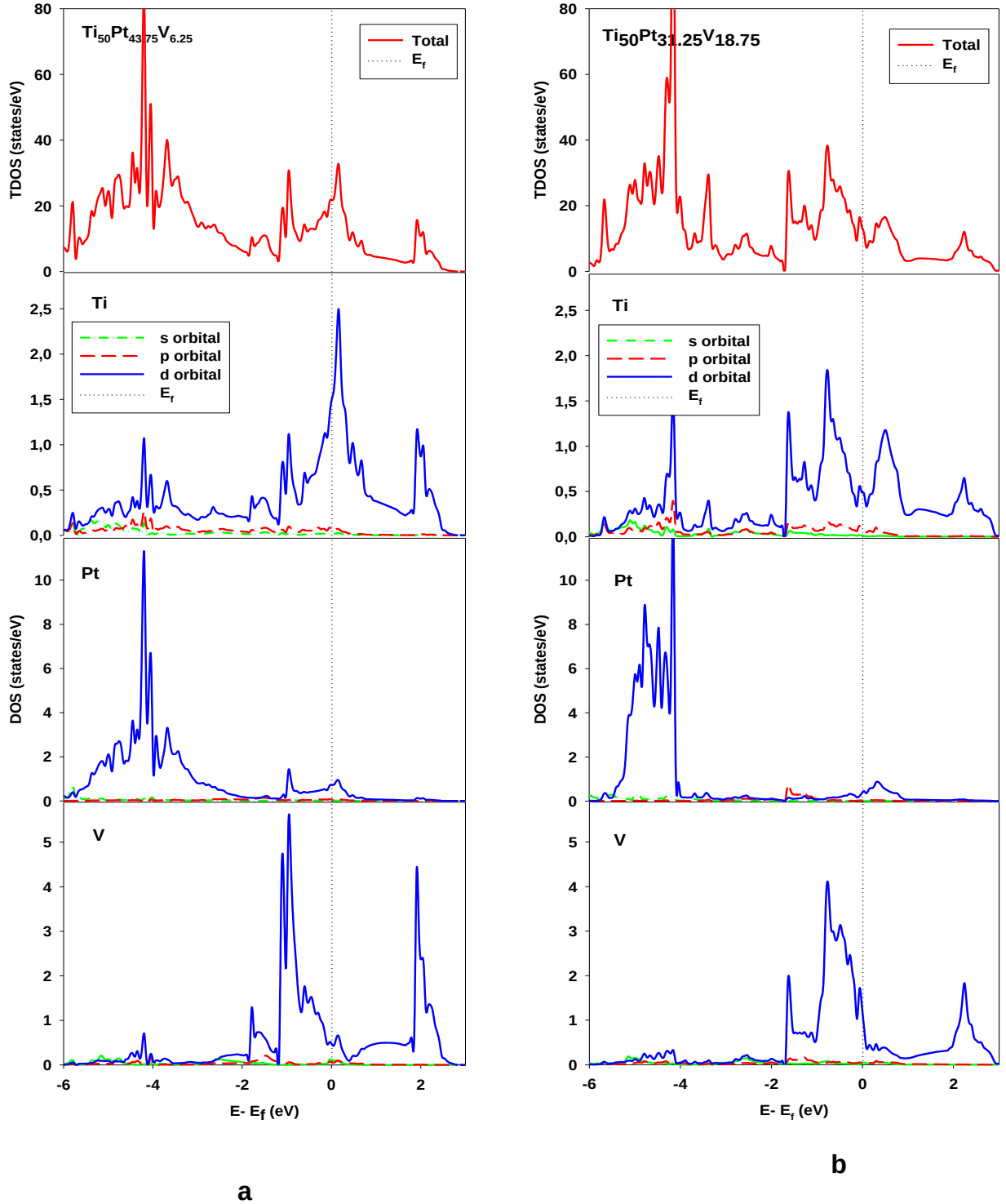


Figure 23. Total and partial density of states for (a). $\text{Ti}_{50}\text{Pt}_{43.75}\text{V}_{6.25}$ and (b). $\text{Ti}_{50}\text{Pt}_{31.25}\text{V}_{18.75}$.

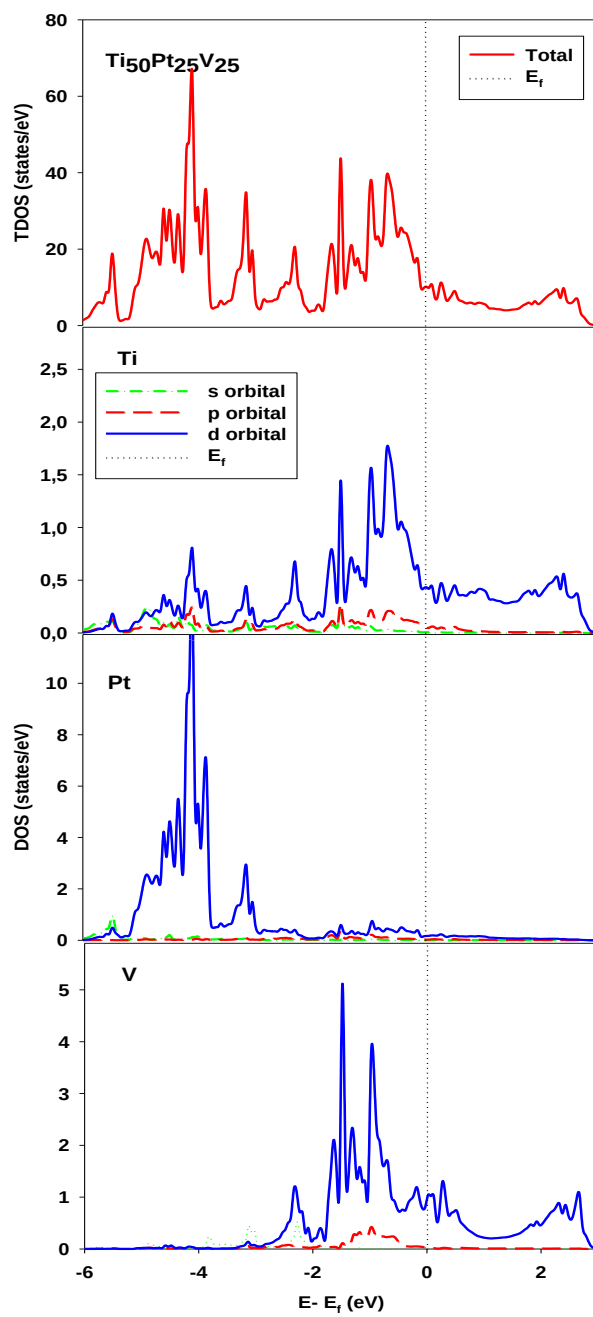


Figure 24. Total and partial density of states for $\text{Ti}_{50}\text{Pt}_{25}\text{V}_{25}$.

In summary, we have plotted the tDOS of V addition in Figure 25 and observe precisely the behaviour at E_f . $\text{Ti}_{50}\text{Pt}_{43.75}\text{V}_{6.25}$ is found to be the most stable structure since it has a lower number of DOS at the E_f . At $x = 18.75$ at.% V, the Fermi level hit the DOS at the shoulder of the dropping peak. Finally, 25 at.% V was found to be less favourable as compared to other concentrations. It is seen that the system becomes unfavourable as V content increases, which is in support with the predicted heats of formation.

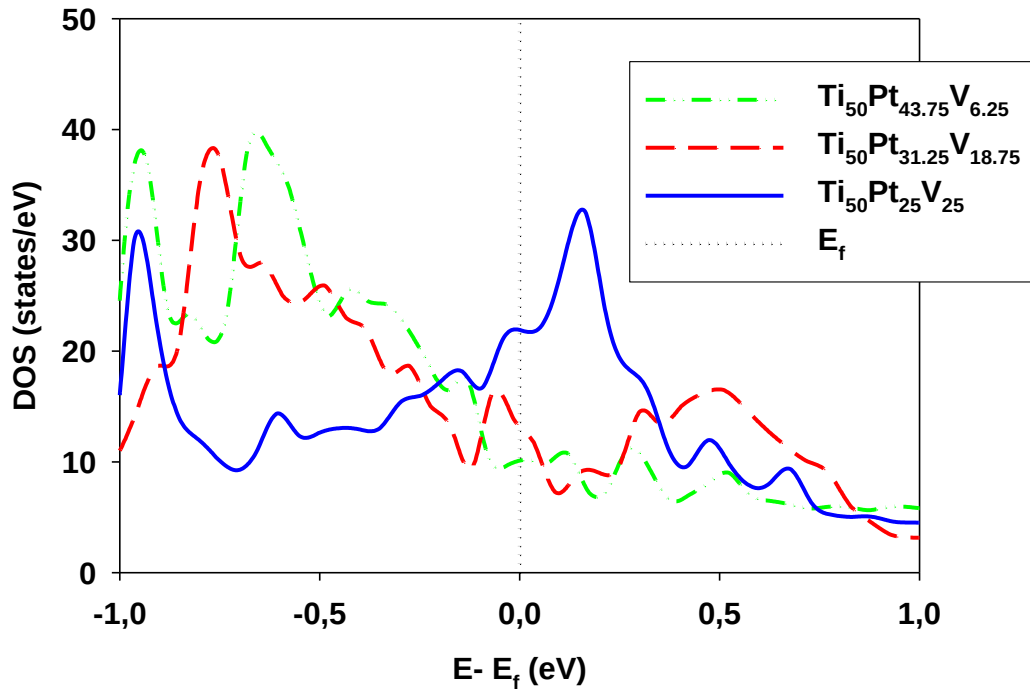


Figure 25. Total density of states for $\text{Ti}_{50}\text{Pt}_{50-x}\text{V}_x$ ($x = 6.25, 18.75, 25$ at.%).

Figures 26 and 27 show the total and partial DOS of $\text{Ti}_{50}\text{Pt}_{50-x}\text{Ta}_x$ alloys at different concentration. In Figure 26, we present the total and partial DOS for (a) $\text{Ti}_{50}\text{Pt}_{43.75}\text{Ta}_{6.25}$ and (b) $\text{Ti}_{50}\text{Pt}_{31.25}\text{Ta}_{18.75}$. In Figure 26 (a), the dominant peak is observed in the valence

band for $\text{Ti}_{50}\text{Pt}_{43.75}\text{Ta}_{6.25}$. At about -4 eV, we note a dominant peak which is a contribution of mainly Pt d-states and less contribution of Ti and Ta d-states. Another peak at -1 eV is contribution mainly of Ta d-states and less of Pt and Ti d-states. Moreover, the peak observed at the Fermi level is the contribution of Ti d-states. However, there is a peak observed in the conduction band which attributed to Ti d-states contribution. As the addition of Ta is increased to 18.75 at.%, there is a shift of peak towards the valence band as shown in Figure 26 (b). The peak at -4 eV decreases as Ta content increases. We observe that the peak at -1 eV disappear for Pt atom, whereas the contribution is from Ti and Ta d-states. There is a small peak observed at the Fermi level, which is a contribution of Ti and Ta d-states. Moreover, the peak at the conduction band fade.

Now in Figure 27, we observe a shift of peak from -4 eV to -4.5 eV in the valence band which is the contribution mainly from Pt d-states and less of Ti d-states and Ta s-states. A peak observed at -2 eV is the contribution of Ta and Ti d-states. Moreover, there is a peak observed at the E_f which is the contribution of mainly Ti d-states and less of Ta d-states. The peak observed at the E_f , coincide with the E_f . There is a negligible contribution of Pt atoms towards the Fermi level.

In order to compare their stability more precisely, we superimposed the total DOS of the three composition structures as shown in Figure 28. We observe the behaviour of the material at the E_f . It is found that $\text{Ti}_{50}\text{Pt}_{43.75}\text{Ta}_{6.25}$ has the lowest number of DOS at the E_f as compared to 18.75 and 25 at.% Ta. This confirms the stability of the 6.25 at.% Ta as predicted from the heats of formation. Moreover, adding up to 18.75 and 25 at.%

Ta increases the number of DOS at the E_f , which results in reduced stability at these compositions.

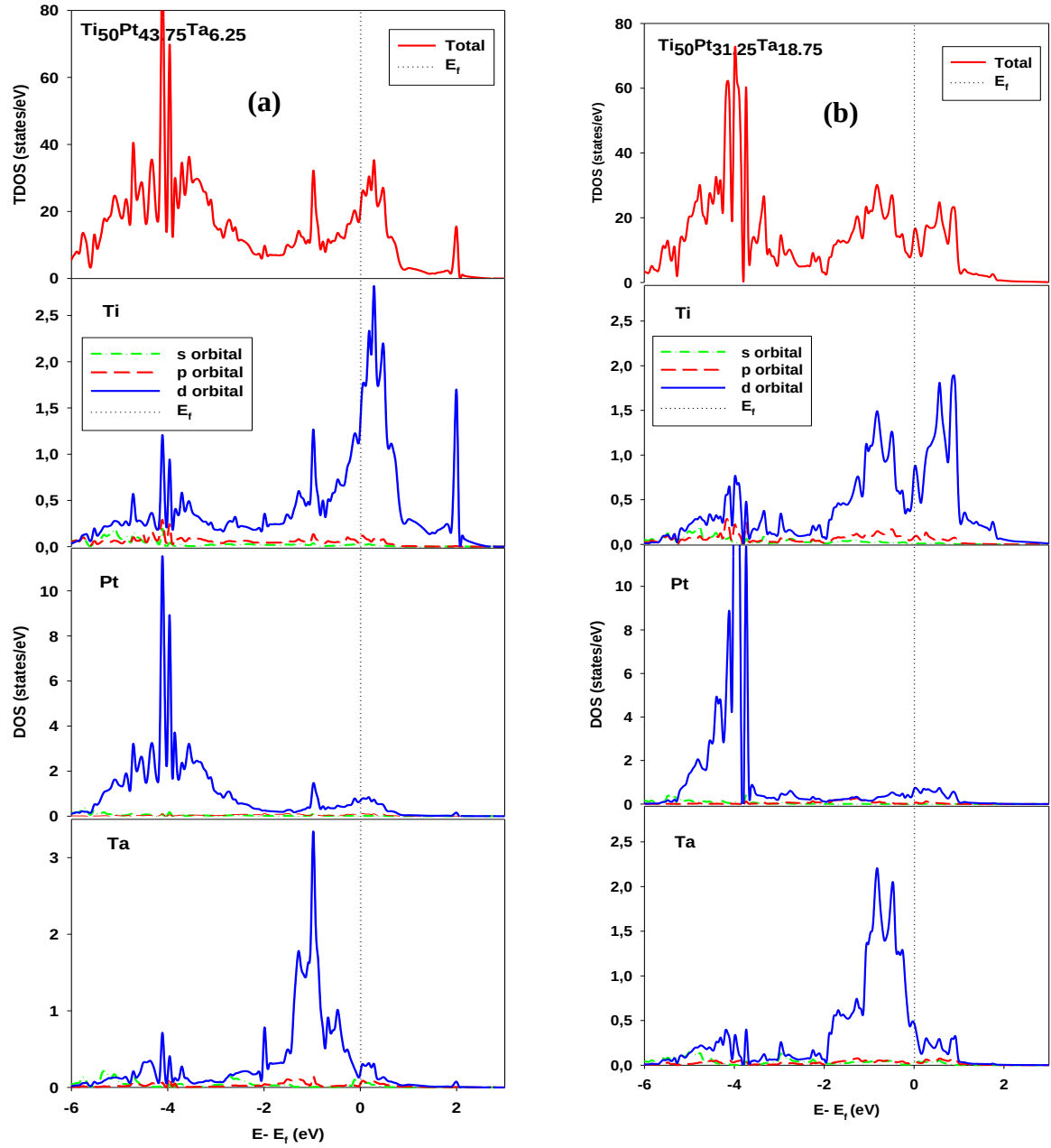


Figure 26. Total and partial density of states for (a) $\text{Ti}_{50}\text{Pt}_{43.75}\text{Ta}_{6.25}$ and (b) $\text{Ti}_{50}\text{Pt}_{31.25}\text{Ta}_{18.75}$.

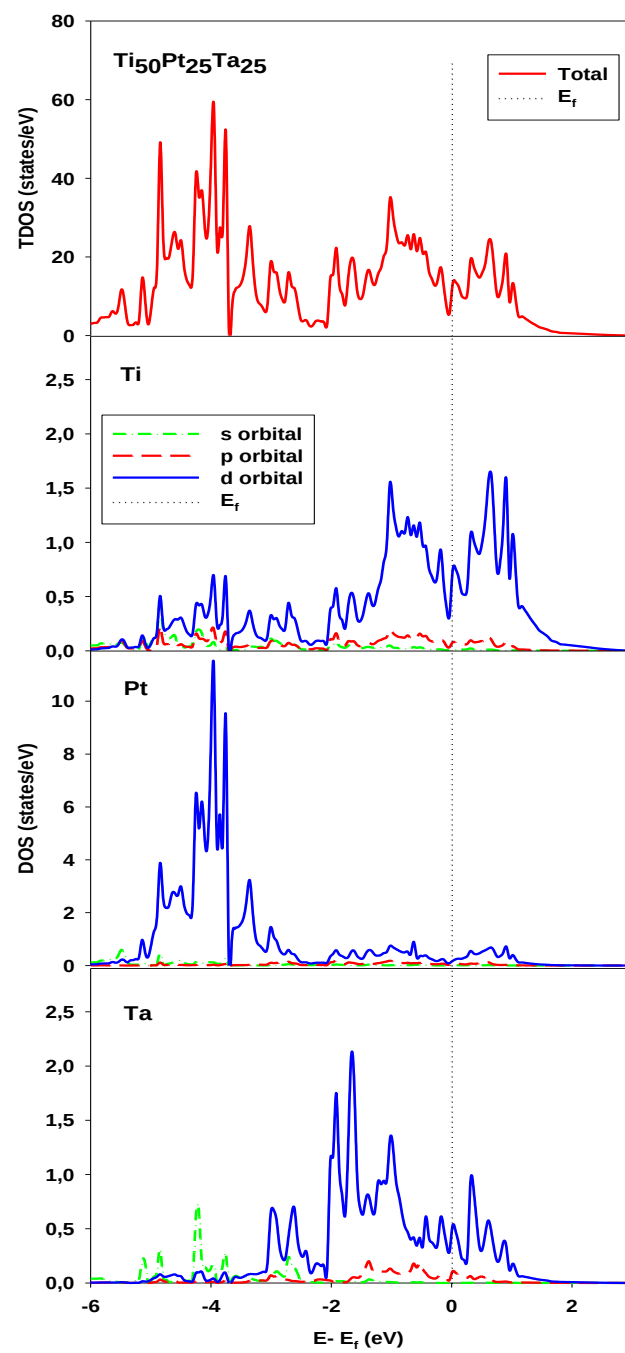


Figure 27. Total and partial density of states for $\text{Ti}_{50}\text{Pt}_{25}\text{Ta}_{25}$.

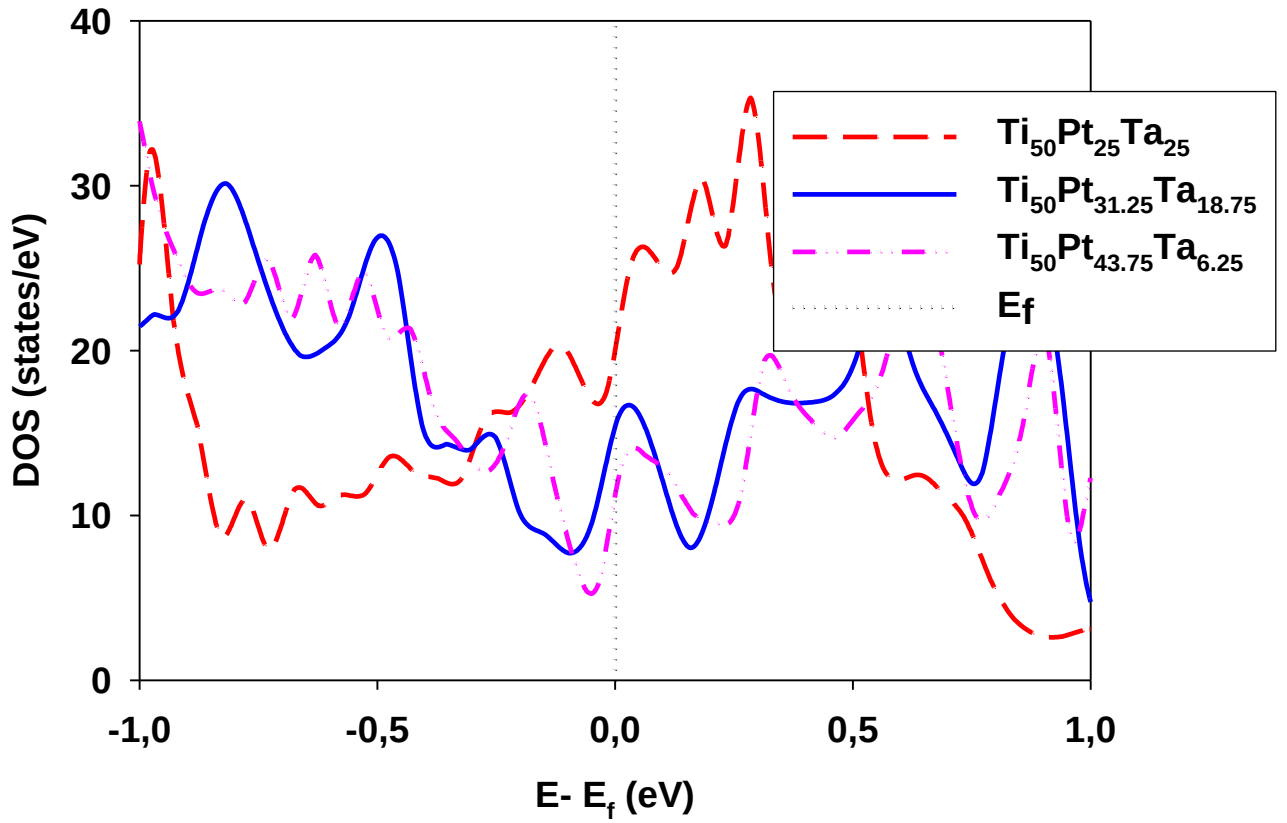


Figure 28. Total density of states for $\text{Ti}_{50}\text{Pt}_{50-x}\text{Ta}_x$ ($x = 6.25, 18.75, 25$).

In Figures 29 and 30, we show the total DOS and PDOS of $\text{Ti}_{50}\text{Pt}_{50-x}\text{Hf}_x$ alloys at different composition. At $x = 6.25$, the dominant peak is observed in the valence band at about -4 eV which is a contribution of mostly Pt d-states and less of Hf and Ti d-states as displayed in Figure 29 (a). The peak at the Fermi level is the contribution of Ti and Hf d-states. Moreover, there are no peaks observed in the conduction band. At 18.75 at.% Hf in Figure 29 (b), some peaks at about -4 eV fade away. Moreover, there is an emerging peak observed at -3 eV which is the contribution of Hf and Ti d-states. However, the peak at the Fermi level broadens and is a contribution from Hf and Ti d-states. At 25 at.% Hf, in Figure 30, the dominant peak is the

contribution of mostly Pt d-states and less of Ti d-states and Hf s-states. Moreover, contribution towards the Fermi level is from Ti and Hf d-states.

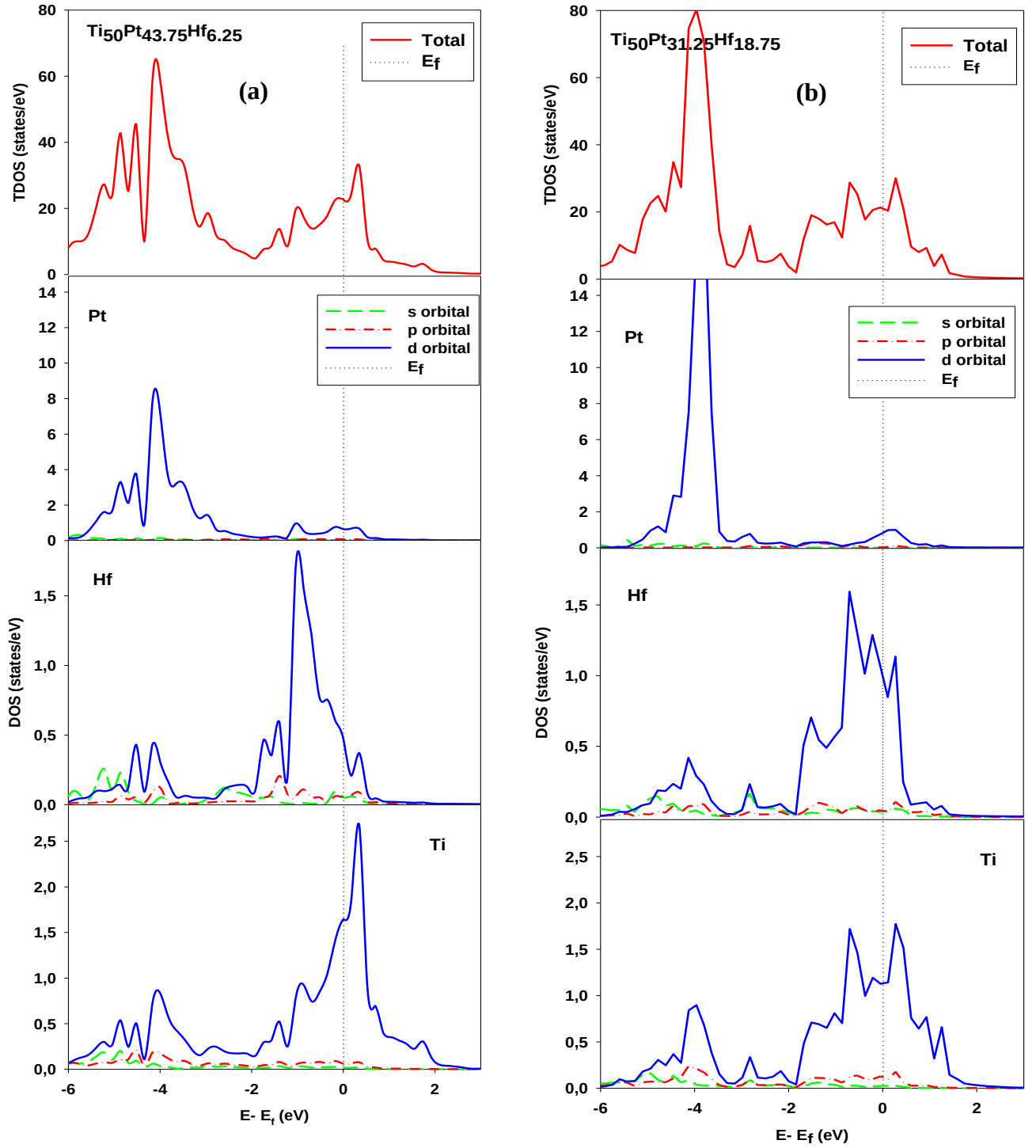


Figure 29. Total and partial density of states for (a) $\text{Ti}_{50}\text{Pt}_{43.75}\text{Hf}_{6.25}$ and (b) $\text{Ti}_{50}\text{Pt}_{31.25}\text{Hf}_{18.75}$.

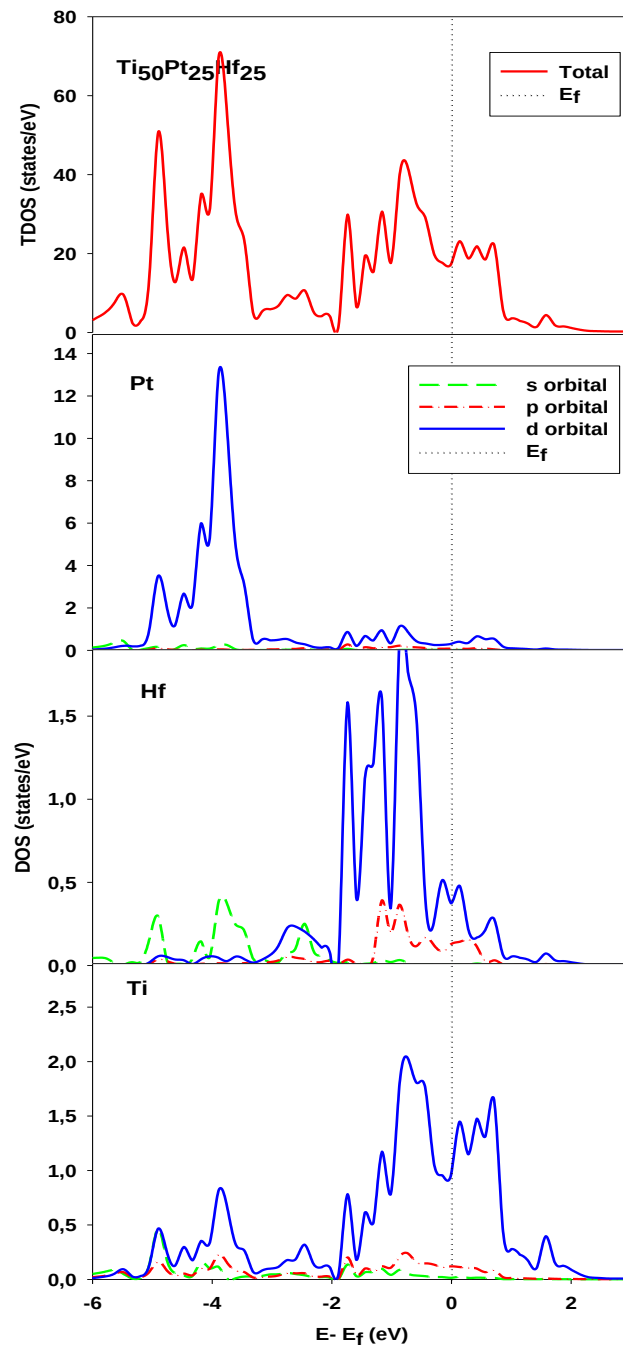


Figure 30. Total and partial density of states for $\text{Ti}_{50}\text{Pt}_{25}\text{Hf}_{25}$.

In summary, we have plotted the total DOS of Hf addition in Figure 31 and observe precisely the behaviour at E_f . It is clear that 6.25 at.% Hf has a lower number of DOS at the E_f as compared to the 18.75 and 25 at.% Hf. We note that as the concentration of Hf is increased in the system, the system becomes less stable with respect to the behaviour of the DOS at the E_f . This confirms the stability of the 6.25 at.% Hf as predicted by the heats of formation. Moreover, the 25 at.% Hf DOS plots are characterized by a broad pseudogap at E_f . Moreover, it was reported that as the content is increased, the structures become unstable. $Ti_{50}Pt_{43.75}Co_{6.25}$ has the lowest number suggesting that stability as compared to $Ti_{50}Pt_{25}Co_{25}$ which has a higher number of DOS at E_f . These results are consistent with the reported heats of formation.

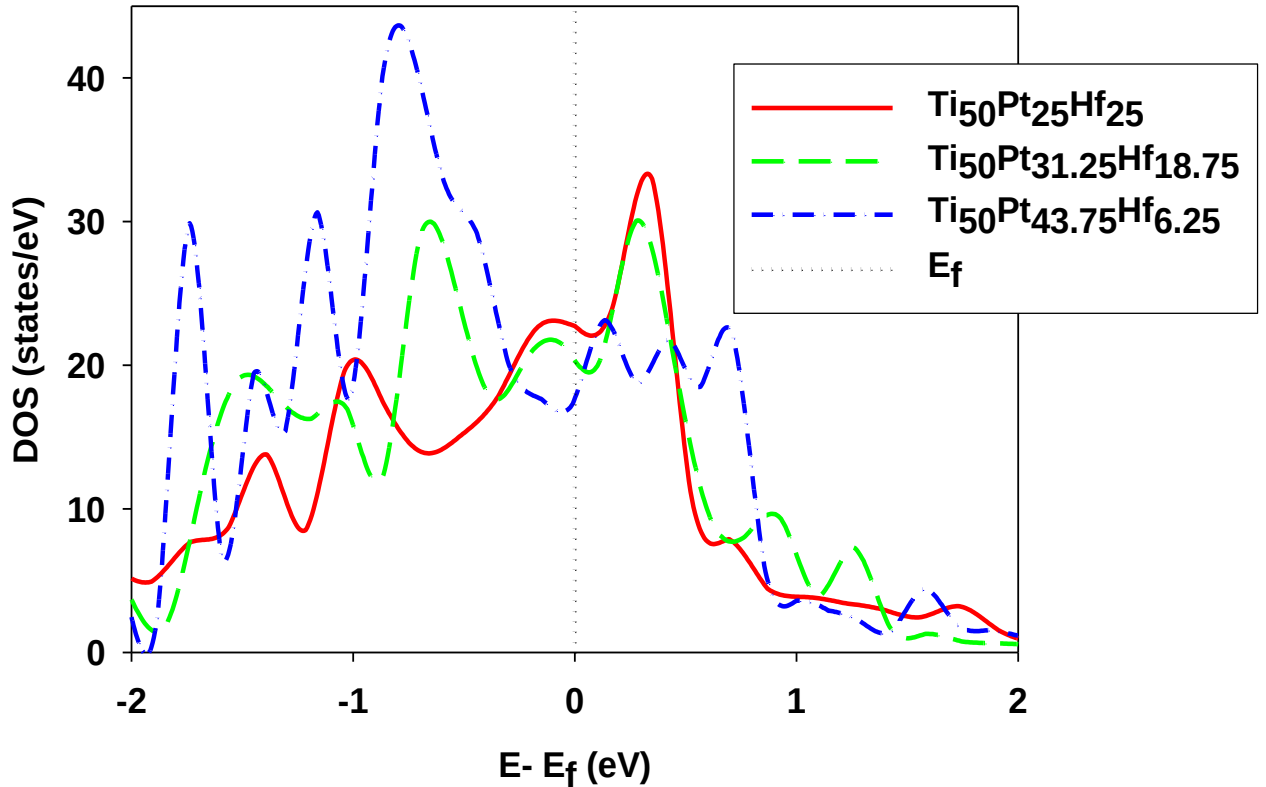


Figure 31. Total density of states for $Ti_{50}Pt_{50-x}Hf_x$ ($x = 6.25, 18.75, 25$).

5.5. Summary

In this chapter, we presented the first principle study on the effect of V, Ta and Hf addition on B2 TiPt binary alloys. The equilibrium lattice parameters of the TiPtM (M = V, Ta, Hf) ternary alloys had been performed within the generalised gradient approximation. Lattice parameters of TiPt decrease with an increase in V concentration, while it increases with an increase in Ta and Hf content in the system, this is because of their difference in atomic radius. The heats of formations endorse that the systems are stable and gave low negative values.

The calculated elastic properties of TiPtM (M = V, Ta, Hf) ternary alloys indicated that the systems are mechanically stable because they satisfy the cubic stability criteria. The shear modulus of TiPt ($C' = -32$) becomes positive with the addition of the third element V, Ta and Hf. This suggests that these alloying elements stabilize the TiPt while decreases the martensitic transformation temperature. The experimental findings showed that the vanadium addition to TiPt decreases its martensitic transformation temperature [56]. This behaviour is in good agreement with our calculated elastic properties. Furthermore, all the ternary alloys investigated in this study are ductile considering that $B/G > 1.75$.

Phonon dispersions indicate that the structures are stable at $x = 18.75$ because of the absence of soft modes (modes in the negative frequency) that are in good agreement with calculated elastic properties that are all positive. The calculations at the phonon dispersion and the density of states were done to confirm the stability of TiPtM (M = V, Ta, Hf) ternary alloys. Previous work showed that the addition of Co to B2 TiPt decreases

the transformation temperature. Furthermore, it was reported that the structure is vibrationally unstable since it displayed soft modes along high symmetry direction of the Brillouin zone (Bz) [53]. The findings show that the addition of Co, V, Ta and Hf stabilizes the B2 TiPt alloys, but decreases the martensitic transformation temperature of TiPt.

The calculated electronic density of states was used to investigate the stability of the materials by exploring the behaviour at the Fermi level with respect to the pseudogap. It was noticed that when the content of V, Ta and Hf is increased in the system, TiPt becomes less stable since the states are high at E_f . Furthermore, the 6.25 at.% Ta, V, Hf addition has lower DOS values at the E_f and it is considered more stable while 25 at.% composition has the highest DOS value which is considered least stable for V, Ta and Hf ternary addition. These analyses are consistent with the heats of formation predictions in section 5.1. Moreover, the phonon DOS revealed that the vibration of Pt atoms are responsible for the stability observed for 6.25 at.% V, Ta and Hf as compared to 18.75 and 25 at.% composition.

CHAPTER 6

TiPtCo-Ta QUATERNARY ALLOYS

In this chapter, we investigate the effect of quaternary alloying of $\text{Ti}_{50}\text{Pt}_{50-x}\text{Co}_x$ with tantalum (Ta) to investigate the stability of the alloy. Previously, the $\text{Ti}_{50}\text{Pt}_{50-x}\text{Co}_x$ ternary alloy (with atomic percent composition of 6.25, 18.75 and 25) was reported to have promising shape memory properties [22, 53]. These alloys were observed to be thermodynamically stable due to their low heats of formation ($\Delta H_f < 0$), with 6.25 at.% Co been the most favourable as discussed in Chapters 2 and 5. Moreover, $\text{Ti}_{50}\text{Pt}_{50-x}\text{Co}_x$ ($x = 6.25, 18.75$ and 25) was found to be mechanically stable since it satisfied the cubic stability criterion. The experimental and computational findings showed that addition of Co on B2 $\text{Ti}_{50}\text{Pt}_{50}$ reduces the martensitic transformation temperature [17, 53]. It was also found that the ternary $\text{Ti}_{50}\text{Pt}_{50-x}\text{Co}_x$ is vibrational unstable at 6.25 at.%. Thus quaternary alloying had been recommended to improve the martensitic transformation temperature and mechanical properties of $\text{Ti}_{50}\text{Pt}_{50-x}\text{Co}_x$ (6.25 and 18.75 at.%) by addition of the fourth element. Note that the Ta addition is on the Pt sublattice, which means that any amount of Ta added the Pt concentration reduces by that amount. The effect of Ta addition on $\text{Ti}_{50}\text{Pt}_{43.75-x}\text{Co}_{6.25}\text{Ta}_x$ and $\text{Ti}_{50}\text{Pt}_{31.25-x}\text{Co}_{18.75}\text{Ta}_x$ ($x = 6.25, 12.50, 18.75$) is investigated wherein their equilibrium lattice parameters, elastic properties, phonon dispersions and density of states are determined. Furthermore, the temperature dependence on the lattice parameters and X-ray diffraction for the $\text{Ti}_{50}\text{Pt}_{43.75-x}\text{Co}_{6.25}\text{Ta}_x$ and $\text{Ti}_{50}\text{Pt}_{31.25-x}\text{Co}_{18.75}\text{Ta}_x$ ($x = 6.25, 18.75, 25$) structures will also be discussed.

6.1. Stability: B2 TiPtCo-Ta alloys

In this section, we discuss the results on the stability of the B2 $\text{Ti}_{50}\text{Pt}_{43.75-x}\text{Co}_{6.25}\text{Ta}_x$ and $\text{Ti}_{50}\text{Pt}_{31.25-x}\text{Co}_{18.75}\text{Ta}_x$ ($x = 6.25, 12.50$ and 18.75) structures. The stability of the structures is determined in terms of their equilibrium lattice parameter, elastic properties, phonon dispersions and density of states.

6.1.1. Structural and thermodynamic properties for B2 TiPtCo-Ta

In Table 6, the calculated equilibrium lattice parameters and heats of formation are shown. It is observed that the addition of Ta increases the lattice parameters of $\text{Ti}_{50}\text{Pt}_{37.50}\text{Co}_{6.25}\text{Ta}_{6.25}$ (from 3.1490 to 3.1565 Å) and $\text{Ti}_{50}\text{Pt}_{25}\text{Co}_{18.75}\text{Ta}_{6.25}$ (from 3.1040 to 3.1082 Å). The lattice parameter decreases for $\text{Ti}_{50}\text{Pt}_{43.75-x}\text{Co}_{6.25}\text{Ta}_x$ and $\text{Ti}_{50}\text{Pt}_{31.25-x}\text{Co}_{18.75}\text{Ta}_x$ with an increase in Ta content as can be seen in Table 6. This is an indication that an increase in Ta content in the system, has a negligible effect in the lattice parameter of the structure since the difference is small. This is due to the large atomic radius of Ta atom as compared to that of the Pt atom. The calculated heats of formation of the systems suggest that as the Ta content is increased, the B2 TiPtCo becomes less stable with an increasing ΔH_f as can be seen in Table 6. The $\text{Ti}_{50}\text{Pt}_{37.50}\text{Co}_{6.25}\text{Ta}_{6.25}$ and $\text{Ti}_{50}\text{Pt}_{25}\text{Co}_{18.75}\text{Ta}_{6.25}$ structures were found to be the most stable with ΔH_f of -0.81 and -0.62 eV/atom; respectively. $\text{Ti}_{50}\text{Pt}_{25}\text{Co}_{6.25}\text{Ta}_{18.75}$ and $\text{Ti}_{50}\text{Pt}_{18.75}\text{Co}_{18.75}\text{Ta}_{12.50}$ were the least stable systems since the structure displayed a high ΔH_f value. In both cases the 6.25 at.% Ta is the most stable phase.

Table 6. Equilibrium lattice parameters (Å) and heats of formation (eV/atom) of B2 $\text{Ti}_{50}\text{Pt}_{43.75-x}\text{Co}_{6.25}\text{Ta}_x$ and $\text{Ti}_{50}\text{Pt}_{31.25-x}\text{Co}_{18.75}\text{Ta}_x$.

B2 Phase	Structures	a	ΔH_f
$\text{Ti}_{50}\text{Pt}_{43.75-x}\text{Co}_{6.25}\text{Ta}_x$	$\text{Ti}_{50}\text{Pt}_{43.75}\text{Co}_{6.25}$	3.1490	-0.74
	$\text{Ti}_{50}\text{Pt}_{37.50}\text{Co}_{6.25}\text{Ta}_{6.25}$	3.1565	-0.81
	$\text{Ti}_{50}\text{Pt}_{25}\text{Co}_{6.25}\text{Ta}_{18.75}$	3.1544	-0.55
$\text{Ti}_{50}\text{Pt}_{31.25-x}\text{Co}_{18.75}\text{Ta}_x$	$\text{Ti}_{50}\text{Pt}_{31.25}\text{Co}_{18.75}$	3.1040	-0.61
	$\text{Ti}_{50}\text{Pt}_{25}\text{Co}_{18.75}\text{Ta}_{6.25}$	3.1082	-0.62
	$\text{Ti}_{50}\text{Pt}_{18.75}\text{Co}_{18.75}\text{Ta}_{12.50}$	3.1080	-0.55

6.1.2. Elastic constants for B2 TiPtCo-Ta

In order to investigate the mechanical stability of the quaternary phases, their elastic constants are calculated as presented in Table 7. The calculated elastic constants are all positive for the $\text{Ti}_{50}\text{Pt}_{43.75-x}\text{Co}_{6.25}\text{Ta}_x$ and $\text{Ti}_{50}\text{Pt}_{31.25-x}\text{Co}_{18.75}\text{Ta}_x$ confirming the stability of the structures at 0 K. As the Ta content is increased from 6.25 to 18.75 at.% in the ($\text{Ti}_{50}\text{Pt}_{43.75-x}\text{Co}_{6.25}\text{Ta}_x$) system, the shear modulus C' decreases which suggest that the transformation temperature of the structure is likely to increase for $\text{Ti}_{50}\text{Pt}_{43.75-x}\text{Co}_{6.25}\text{Ta}_x$ alloys. Moreover, C' increases as Ta is increased from 6.25 to 12.50 at.% for the $\text{Ti}_{50}\text{Pt}_{31.25-x}\text{Co}_{18.75}\text{Ta}_x$ system which suggest that transformation temperature is likely to decrease. Similarly, for $\text{Ti}_{50}\text{Pt}_{25}\text{Co}_{18.75}\text{Ta}_{6.25}$ and $\text{Ti}_{50}\text{Pt}_{18.75}\text{Co}_{18.75}\text{Ta}_{12.50}$, systems are found to be mechanically stable since they satisfy cubic stability criteria. We have also calculated the elastic anisotropy, A which is used to correlate the possibility to induce micro-cracks in the materials [70]. We note that the A value of $\text{Ti}_{50}\text{Pt}_{43.75-x}\text{Co}_{6.25}\text{Ta}_x$ is less than 1. The A value for $\text{Ti}_{50}\text{Pt}_{18.75}\text{Co}_{18.75}\text{Ta}_{12.50}$ is 0.94 which suggest less micro-cracks in

the material while for $\text{Ti}_{50}\text{Pt}_{25}\text{Co}_{18.75}\text{Ta}_{6.25}$, A is 1.50 which is lower as compared to that of TiNi ($A = 2.40$) [138].

Table 7. Elastic properties (C_{ij} 's (GPa)), Bulk (B), Shear (G), Young's (E) and Pugh's ratio (B/G) of B2 $\text{Ti}_{50}\text{Pt}_{43.75-x}\text{Co}_{6.25}\text{Ta}_x$ and $\text{Ti}_{50}\text{Pt}_{31.25-x}\text{Co}_{18.75}\text{Ta}_x$.

Structures	$\text{Ti}_{50}\text{Pt}_{43.75-x}\text{Co}_{6.25}\text{Ta}_x$		$\text{Ti}_{50}\text{Pt}_{31.25-x}\text{Co}_{18.75}\text{Ta}_x$	
At.% Ta	6.25	18.75	6.25	12.50
C_{11}	290	267	234	244
C_{12}	131	148	155	126
C_{44}	60	29	60	55
C'	80	60	40	59
A	0.75	0.48	1.50	0.94
B	184	187	181	166
G	67	39	51	57
E	180	108	139	152
B/G	2.74	4.87	3.57	2.94

We have also calculated the Bulk, Shear, Young's modulus and Pugh's ratio of $\text{Ti}_{50}\text{Pt}_{43.75-x}\text{Co}_{6.25}\text{Ta}_x$ are shown in Table 7. $\text{Ti}_{50}\text{Pt}_{25}\text{Co}_{6.25}\text{Ta}_{18.75}$ has the highest bulk modulus, which indicates that the material is more resistant to compression as compared to $\text{Ti}_{50}\text{Pt}_{37.50}\text{Co}_{6.25}\text{Ta}_{6.25}$. The $\text{Ti}_{50}\text{Pt}_{25}\text{Co}_{18.75}\text{Ta}_{6.25}$ alloy is found to be more resistant to compression as compared to $\text{Ti}_{50}\text{Pt}_{18.75}\text{Co}_{18.75}\text{Ta}_{12.50}$ due to high bulk moduli. Now, recall that low values of Young's modulus suggest the structures flexibility and easy to bend or elastic where high values are associated with high stiffness [139]. These current findings suggest that $\text{Ti}_{50}\text{Pt}_{25}\text{Co}_{6.25}\text{Ta}_{18.75}$ is less stiff since it has low Young's moduli. Moreover, $\text{Ti}_{50}\text{Pt}_{25}\text{Co}_{18.75}\text{Ta}_{6.25}$ is also found to be less stiff. In addition, $\text{Ti}_{50}\text{Pt}_{25}\text{Co}_{6.25}\text{Ta}_{18.75}$ appears to be more rigid due to its high shear modulus. As the content of Ta increases (18.75 at.%)

Ta) in the system, the shear modulus decreases (39 GPa). $\text{Ti}_{50}\text{Pt}_{25}\text{Co}_{18.75}\text{Ta}_{6.25}$ is more flexible compared to $\text{Ti}_{50}\text{Pt}_{18.75}\text{Co}_{18.75}\text{Ta}_{12.50}$.

All the quaternary alloys investigated are ductile since their Pugh's ratio is greater than the critical value. Moreover, $\text{Ti}_{50}\text{Pt}_{25}\text{Co}_{6.25}\text{Ta}_{18.75}$ is more ductile since it has high B/G (4.87) ratio as compared to $\text{Ti}_{50}\text{Pt}_{37.50}\text{Co}_{6.25}\text{Ta}_{6.25}$ (B/G = 2.74). Furthermore, $\text{Ti}_{50}\text{Pt}_{25}\text{Co}_{18.75}\text{Ta}_{6.25}$ and $\text{Ti}_{50}\text{Pt}_{18.75}\text{Co}_{18.75}\text{Ta}_{12.50}$ were also found to be ductile displaying values greater than 1.75.

6.1.3. Phonon dispersions for B2 TiPtCo-Ta

In Figures 32 and 33, the phonon dispersions and phonon density of states (PDOS) plots for different concentration of $\text{Ti}_{50}\text{Pt}_{43.75-x}\text{Co}_{6.25}\text{Ta}_x$ quaternary alloys are shown. It is noted from the phonon dispersion curves that $\text{Ti}_{50}\text{Pt}_{37.50}\text{Co}_{6.25}\text{Ta}_{6.25}$ is vibrationally unstable due to soft modes observed along the high symmetry directions in the negative frequency. These soft modes are due to the high vibration of Co and Pt d-states in the system as depicted by the phonon PDOS in Figure 32 (b). Moreover, the phonon DOS indicates that vibrations above 3 THz are due to Ti and Ta d-states considering that they have the highest peaks in the positive frequency, whilst the ones below 3 THz are contributions from the Pt and Co for 6.25 at.% Ta.

In Figure 33, the soft modes disappear as the content is increased to 18.75 at.% Ta which suggest that at this concentration the structure is vibrationally stable. For high content of Ta (18.75 at.%), the vibrations are all above 0 THz. It is seen that Pt and Co peaks shift from the negative frequency to the positive frequency as the Ta content increases in the system. This results in the absence of soft modes which suggest the stability of the

material at this composition. The phonon DOS (Figure 33 (b)) show that Ta, Co and Pt atoms vibrations are dominant at frequency approximately 3.5 THz.

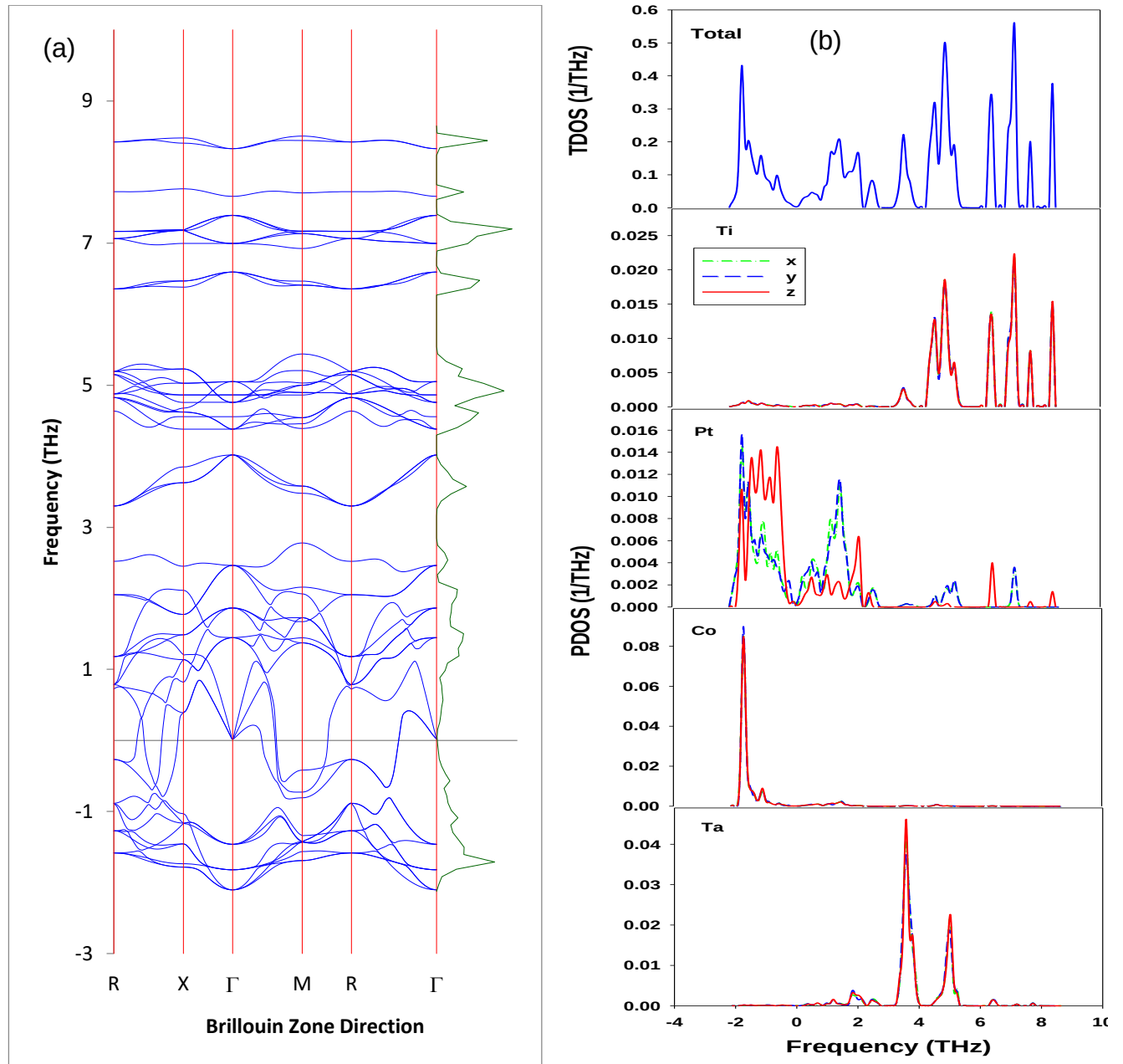


Figure 32. Phonon dispersion (a) and phonon DOS (b) of B2 Ti₅₀Pt_{37.50}Co_{6.25}Ta_{6.25}.

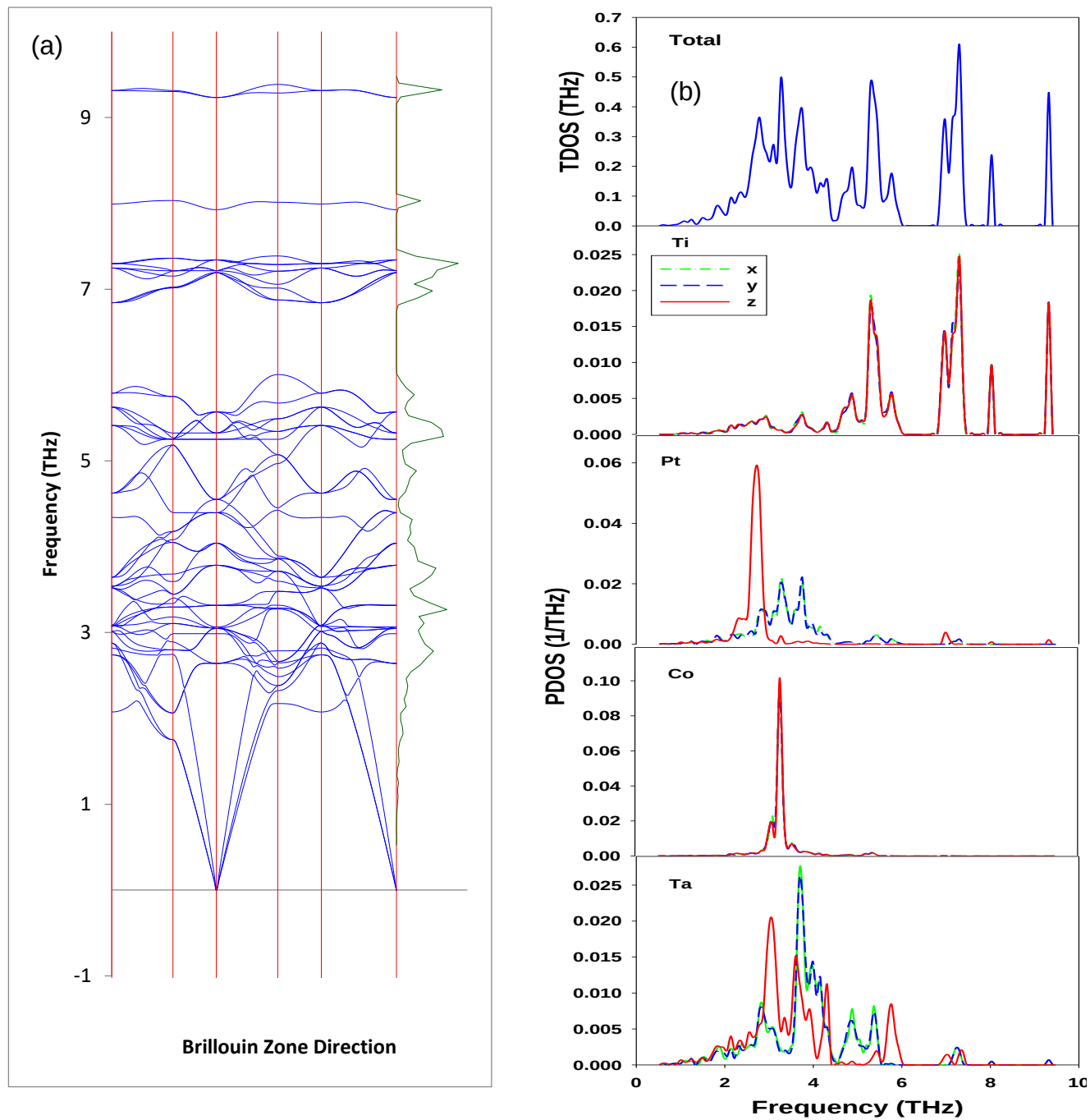


Figure 33. Phonon dispersion (a) and phonon DOS (b) of B2 $\text{Ti}_{50}\text{Pt}_{25}\text{Co}_{6.25}\text{Ta}_{18.75}$.

In Figure 34, the phonon dispersion and phonon density of states for $\text{Ti}_{50}\text{Pt}_{25}\text{Co}_{18.75}\text{Ta}_{6.25}$ are shown. There are soft modes observed in the negative frequency along the R, M and Γ high symmetry directions which suggest that at this concentration (6.25 at.% Ta) the structure is vibrationally unstable. These soft modes observed in the negative frequency are due to the high contribution of Pt in the z-axis. There is a negligible vibration of Ti and Co observed in the negative frequency suggested by phonon DOS as shown in Figure 34 (b).

Furthermore, Figure 35 shows the phonon dispersion and phonon DOS for B2 $\text{Ti}_{50}\text{Pt}_{18.75}\text{Co}_{18.75}\text{Ta}_{12.50}$. It is observed that $\text{Ti}_{50}\text{Pt}_{18.75}\text{Co}_{18.75}\text{Ta}_{12.50}$ is vibrationally stable since there are no soft modes observed in the negative frequency. In Figure 35 (b), the phonon DOS show that there is a shift in vibration of Pt atoms from the negative to positive frequency resulting in the stability of the material. The vibrations found below 8 THz are due to Pt, Co and Ta atoms while above 8 THz is due to Ti atoms. These results are consistent with the calculated elastic constants in Table 7 wherein $\text{Ti}_{50}\text{Pt}_{18.75}\text{Co}_{18.75}\text{Ta}_{12.50}$ was found to be stable.

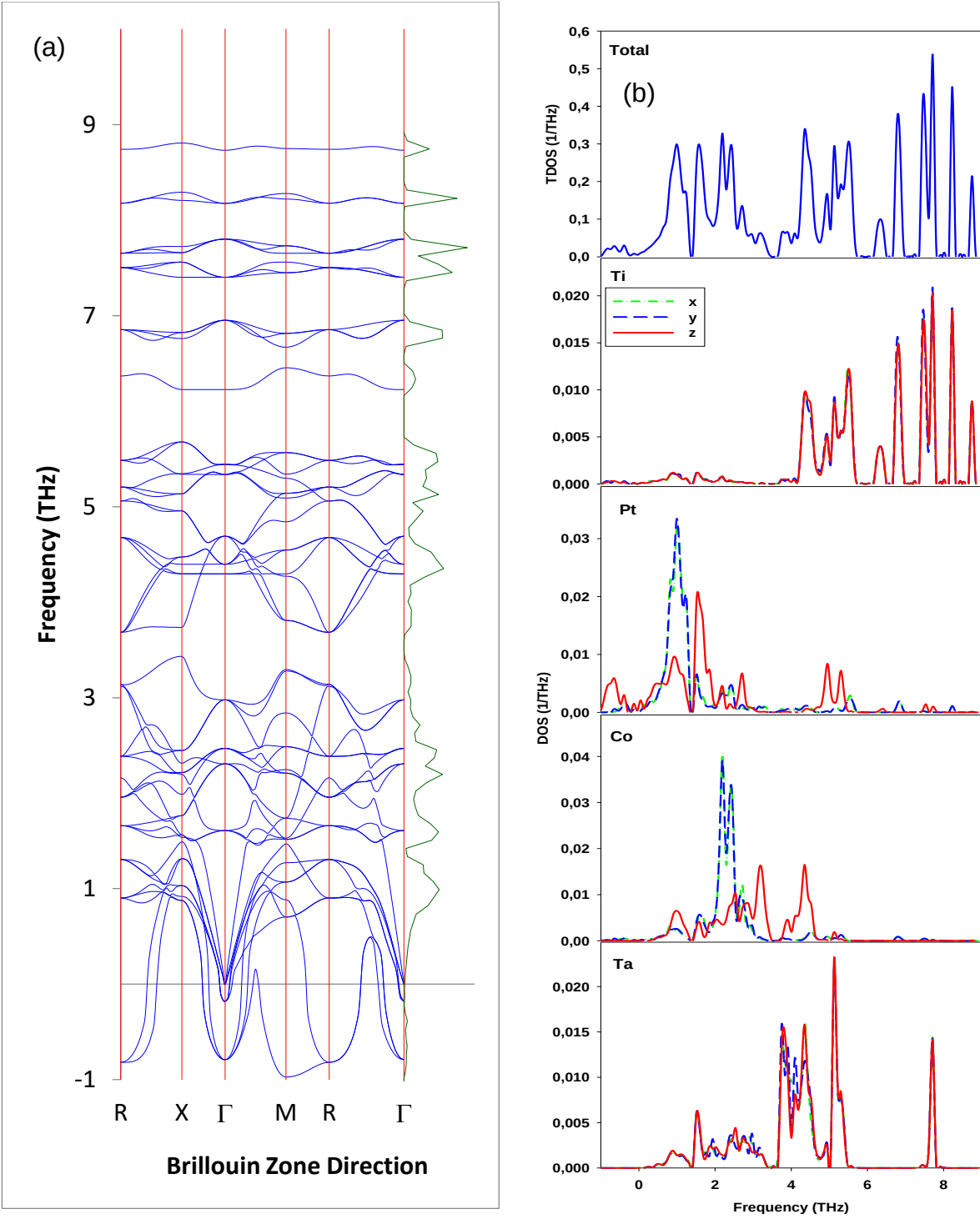


Figure 34. Phonon dispersion (a) and phonon DOS (b) of B2 $\text{Ti}_{50}\text{Pt}_{25}\text{Co}_{18.75}\text{Ta}_{6.25}$.

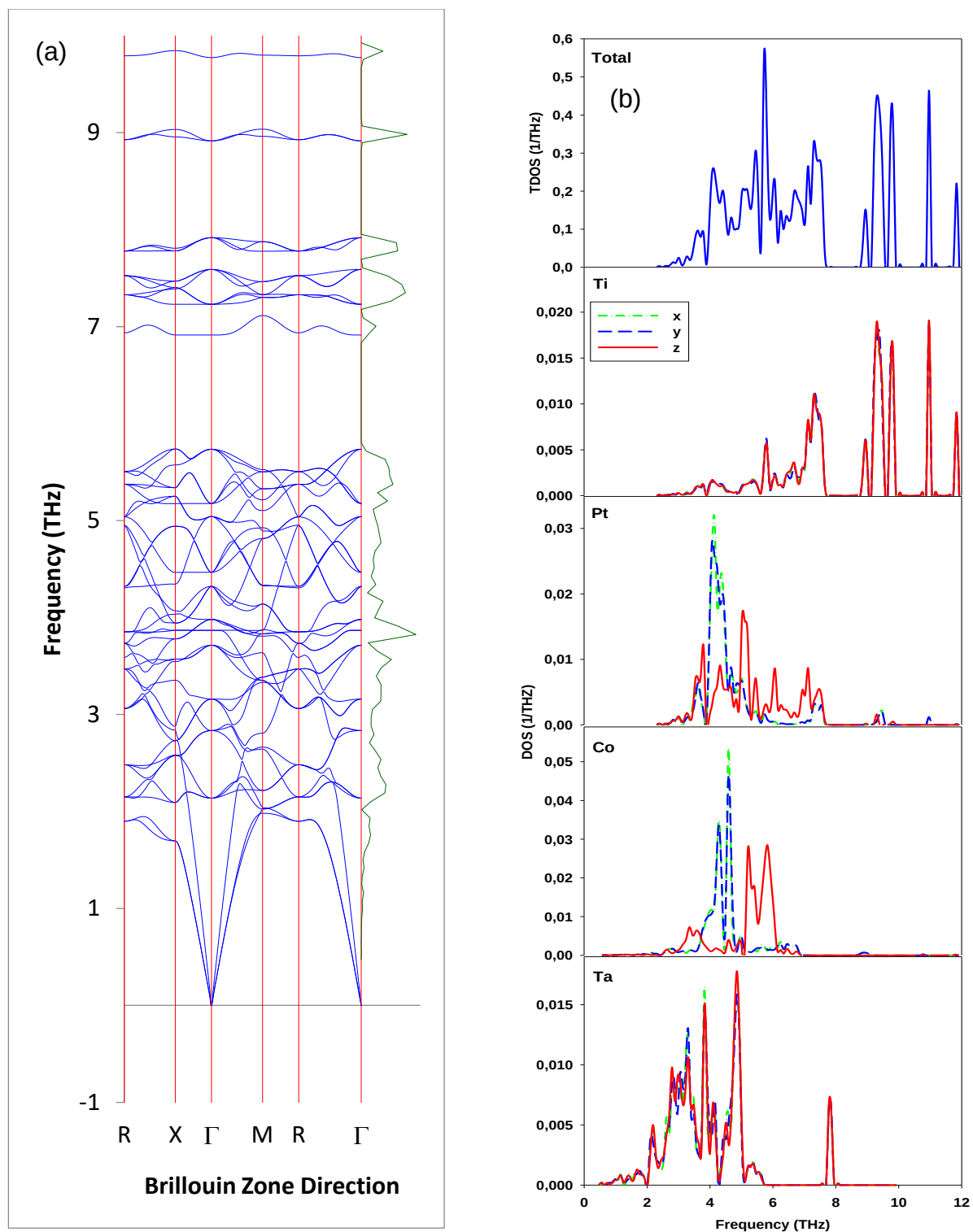


Figure 35. Phonon dispersion (a) and phonon DOS (b) of B2 $\text{Ti}_{50}\text{Pt}_{18.75}\text{Co}_{18.75}\text{Ta}_{12.50}$.

6.1.4. Density of states for B2 TiPtCo-Ta

In Figure 36, the partial and total density of states for the $\text{Ti}_{50}\text{Pt}_{43.75-x}\text{Co}_{6.25}\text{Ta}_x$ is shown. At $x = 6.25$, we observe a dominant peak at -4 eV which is the contribution mainly from Pt d-states and less of Ti, Co and Ta d-states as suggested by the partial DOS in Figure 36 (a). A peak at -2 eV is predominant of Co d-states with less contribution from Ta and Ti d-states. Another peak is observed at about -1 eV which is a contribution of Ti, Pt, Co and Ta d-states. Moreover, there is a high contribution of Ti d-states towards the Fermi level and the peaks at the conduction band.

Further addition of Ta up to 18.75 at.%, we observe the dominant peak at approximately -5 eV, which is mainly Pt d-states contribution as shown in Figure 36 (b). It is noticed that Co d-states are dominant at about -2 eV whereas Ta d-states at approximately -1 eV. We note that the Co d-states peak at -2 eV increases with an increase in Ta content. There is a negligible contribution of Pt and Ta towards the conduction band. Moreover, it is seen that Ti contribute towards the Fermi level and dominant in the conduction band with the observed peak which is mostly characterized by Ti d-states. The peak at 1 eV split into two peaks and peak height decrease.

In order to compare their stability, the tDOS for $\text{Ti}_{50}\text{Pt}_{43.75-x}\text{Co}_{6.25}\text{Ta}_x$ (6.25 and 18.75 at.%) structure were plotted and shown in Figure 37. The tDOS are superimposed in order to relate the stability of the structures at the Fermi level with an addition of tantalum. $\text{Ti}_{50}\text{Pt}_{25}\text{Co}_{6.25}\text{Ta}_{18.75}$ is found to have a lower number DOS at the Fermi level as compared to $\text{Ti}_{50}\text{Pt}_{37.50}\text{Co}_{6.25}\text{Ta}_{6.25}$ and falls into a pseudogap. The $\text{Ti}_{50}\text{Pt}_{25}\text{Co}_{6.25}\text{Ta}_{18.75}$ is found to be more stable with the lowest number of DOS at E_f as compared to $\text{Ti}_{50}\text{Pt}_{37.50}\text{Co}_{6.25}\text{Ta}_{6.25}$.

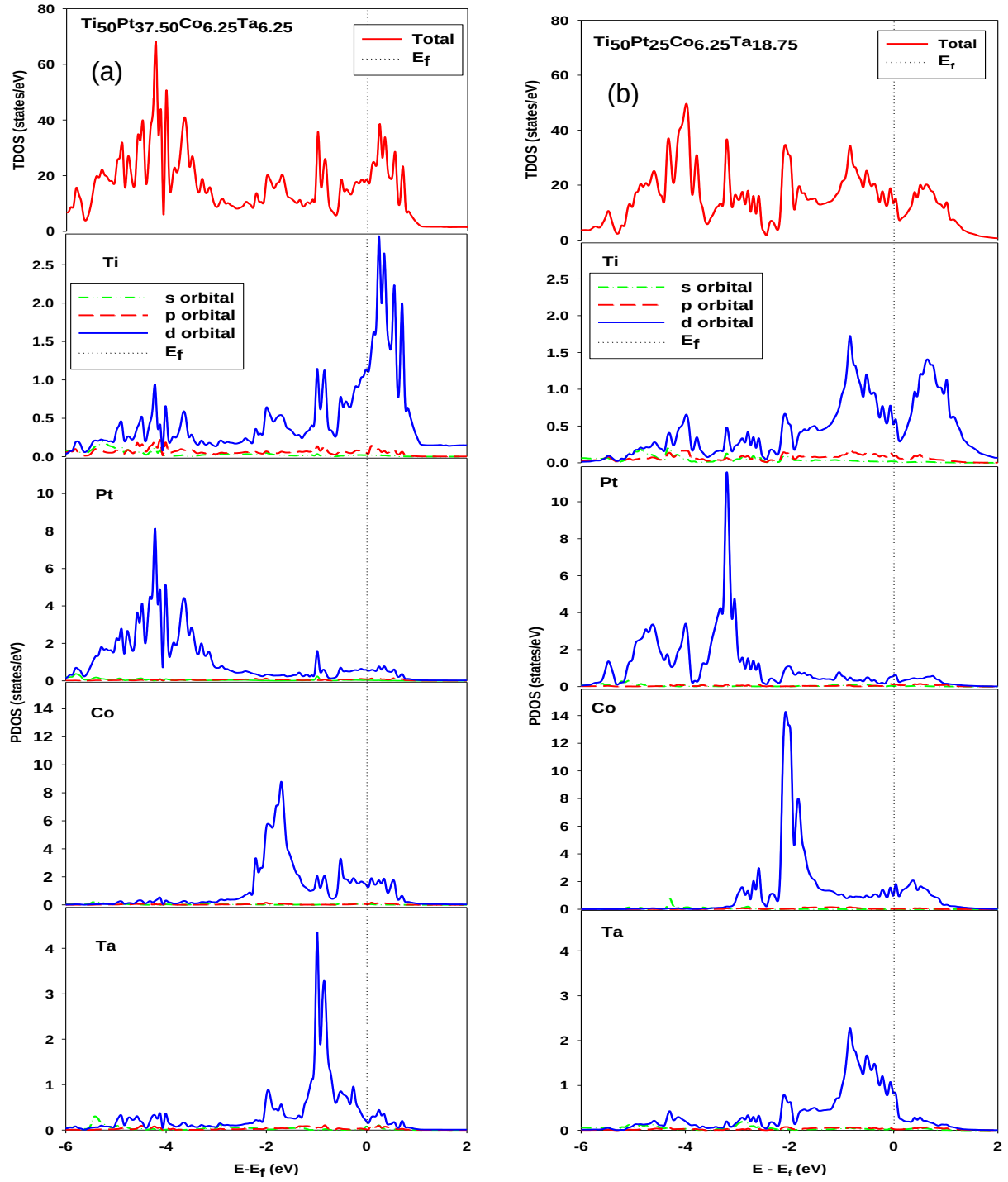


Figure 36. Total and partial density of states for (a) $\text{Ti}_{50}\text{Pt}_{37.5}\text{Co}_{6.25}\text{Ta}_{6.25}$ and (b) $\text{Ti}_{50}\text{Pt}_{25}\text{Co}_{6.25}\text{Ta}_{18.75}$.

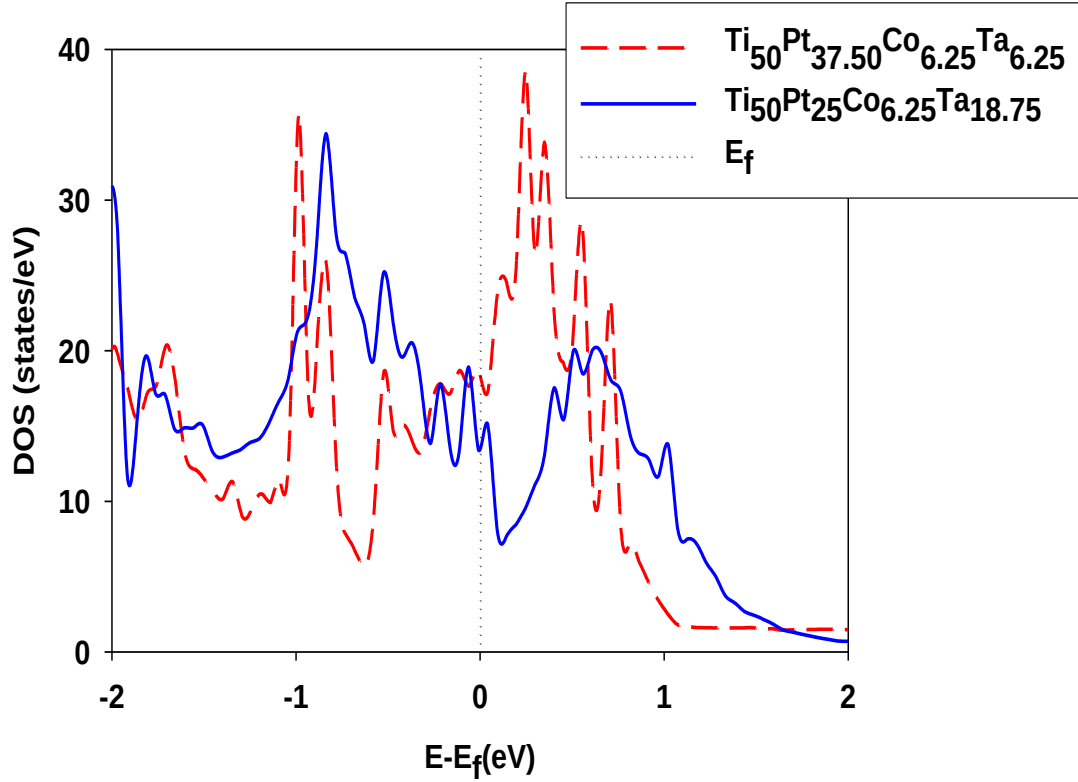


Figure 37. Total density of states for $\text{Ti}_{50}\text{Pt}_{43.75-x}\text{Co}_{6.25}\text{Ta}_x$ ($x = 6.25$ and 18.75 at.%).

In Figure 38, the total and partial density of states for $\text{Ti}_{50}\text{Pt}_{25}\text{Co}_{18.75}\text{Ta}_{6.25}$ and $\text{Ti}_{50}\text{Pt}_{18.75}\text{Co}_{18.75}\text{Ta}_{12.50}$ are shown. We observe a dominant peak in the valence band at approximately -2 eV attributed to Co d-states. We also note that the Pt, Co and Ta d-states are dominant at about -4, -2 and -1 eV, respectively. Moreover, DOS at the Fermi level is characterized by a peak which is a contribution from Ti d-states. However, we observe a peak in the conduction band at 1 eV which is a contribution of mainly Ti d-states.

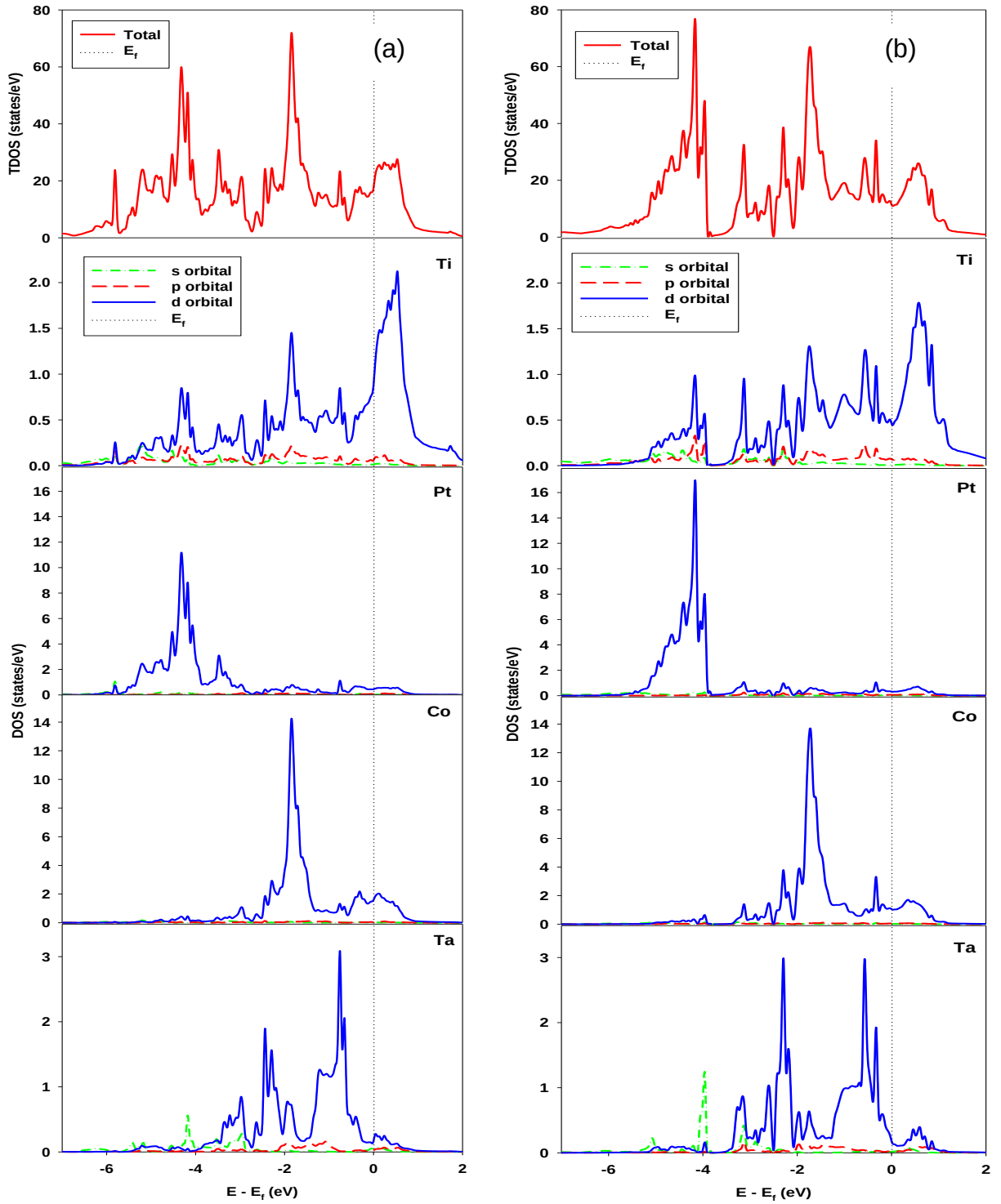


Figure 38. Total and partial density of states of (a) $\text{Ti}_{50}\text{Pt}_{25}\text{Co}_{18.75}\text{Ta}_{6.25}$ and (b) $\text{Ti}_{50}\text{Pt}_{18.75}\text{Co}_{18.75}\text{Ta}_{12.50}$.

In Figure 38 (b), the total and partial DOS of B2 $\text{Ti}_{50}\text{Pt}_{18.75}\text{Co}_{18.75}\text{Ta}_{12.50}$ are presented. There is a high contribution of Pt d-states towards the dominant peak observed at about -4 eV and less of Ti, Co and Ta d-states. It is clearly seen that Pt peak at -4 eV increases with an increase of Ta content from 6.25 to 12.50 at.%. The peak observed at -2.5 eV increases while the peak at -2 eV decreases and slightly shift to -1.9 eV for Co atom as displayed by partial DOS. Moreover, Ta d-states is more dominant at about -1 eV, where the peak slightly decreases with an increase of Ta content to 12.50 at.%. The peak observed at about -4.1 eV which is characterized by Ta s-states shift to -4 eV and increases with an increase in Ta content in the system. The Fermi level is characterized by the peak which is attributed to Ti d-states contribution. Moreover, there is a high contribution of Ti d-states towards the conduction band.

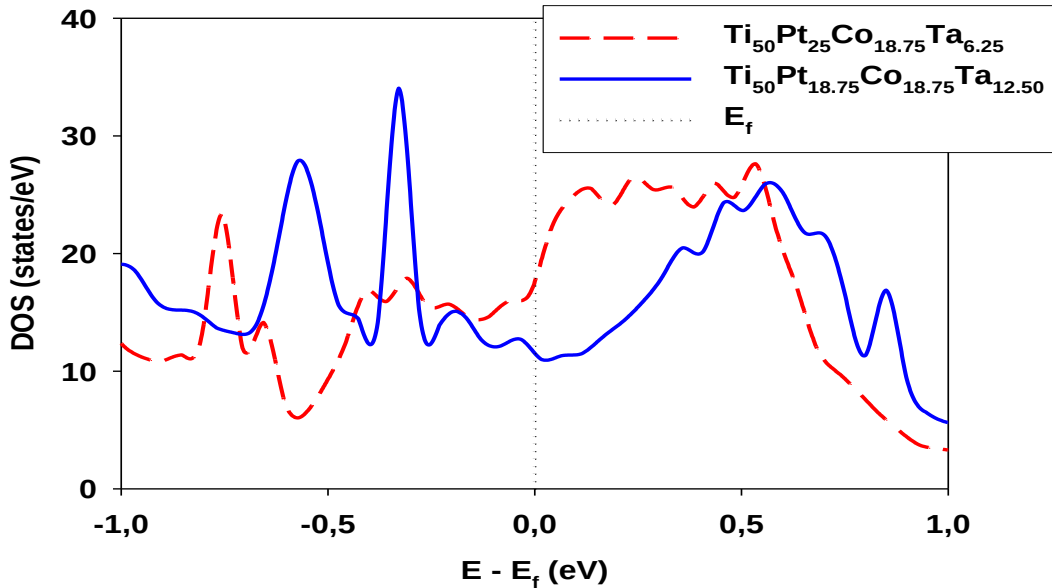


Figure 39. Total density of states for B2 $\text{Ti}_{50}\text{Pt}_{25}\text{Co}_{18.75}\text{Ta}_{6.25}$ and $\text{Ti}_{50}\text{Pt}_{18.75}\text{Co}_{18.75}\text{Ta}_{12.50}$.

Figures 39 show the total DOS of the B2 $\text{Ti}_{50}\text{Pt}_{25}\text{Co}_{18.75}\text{Ta}_{6.25}$ and $\text{Ti}_{50}\text{Pt}_{18.75}\text{Co}_{18.75}\text{Ta}_{12.50}$ quaternary alloys. It is noted that $\text{Ti}_{50}\text{Pt}_{18.75}\text{Co}_{18.75}\text{Ta}_{12.50}$ is the most stable quaternary alloy as compared to $\text{Ti}_{50}\text{Pt}_{25}\text{Co}_{18.75}\text{Ta}_{6.25}$. This is due to the lower number of DOS at the Fermi level as compared to 6.25 at.% Ta, which has a high number of DOS at E_f . We note that as the concentration of Ta is increased in the system, the system becomes more stable with respect to the behaviour of the DOS at the E_f . This is attributed to the decrease in the contribution of Ti d-states towards the E_f as Ta content is increased from 6.25 to 12.50 at.%. These results are inconsistent with the reported heats of formation in section 6.1.1.

6.2. Stability: B19 TiPtCo-Ta alloys

In this section, we discuss the stability of B19 $\text{Ti}_{50}\text{Pt}_{43.75-x}\text{Co}_{6.25}\text{Ta}_x$ and $\text{Ti}_{50}\text{Pt}_{31.25-x}\text{Co}_{18.75}\text{Ta}_x$ alloys. Three compositions for $\text{Ti}_{50}\text{Pt}_{43.75-x}\text{Co}_{6.25}\text{Ta}_x$ alloys are explored that is 6.25, 12.50 and 18.75 at.% Ta whereas for $\text{Ti}_{50}\text{Pt}_{31.25-x}\text{Co}_{18.75}\text{Ta}_x$ two are explored (6.25 and 12.50 at.%). In order to deduce the stability of the structures at various compositions their equilibrium lattice parameter, heats of formation, elastic properties, phonon dispersion and density of states were determined.

6.2.1. Structural and thermodynamic properties for B19 TiPtCo-Ta

In Table 8, the calculated equilibrium lattice parameters and heats of formation for the B19 TiPtCoTa quaternary alloys are shown. For $\text{Ti}_{50}\text{Pt}_{43.75-x}\text{Co}_{6.25}\text{Ta}_x$ alloys, we note that a parameter increases with an increase in Ta content from 6.25 to 12.50 at.% and decreases when $x = 18.75$ at.% Ta. The b and c lattice parameters remain the same as Ta content increase from $x = 6.25$ to 12.50 at.% and further increases when 18.75 at.% Ta was added into the system. For $\text{Ti}_{50}\text{Pt}_{31.25-x}\text{Co}_{18.75}\text{Ta}_x$ alloys, the a and c parameters

decrease with an increase in Ta content from 6.25 to 12.50 at.% while the b parameter increases with an increase in Ta content.

The calculated heats of formation suggest that $\text{Ti}_{50}\text{Pt}_{37.50}\text{Co}_{6.25}\text{Ta}_{6.25}$ is the most stable structure since it has the lowest ΔH_f value of -0.75 eV/atoms while $\text{Ti}_{50}\text{Pt}_{25}\text{Co}_{6.25}\text{Ta}_{18.75}$ is the least stable structure. For $\text{Ti}_{50}\text{Pt}_{31.25-x}\text{Co}_{18.75}\text{Ta}_x$ system, $\text{Ti}_{50}\text{Pt}_{25}\text{Co}_{18.75}\text{Ta}_{6.25}$ ($\Delta H_f = -0.63$ eV/atom) is the most stable structure as compared to $\text{Ti}_{50}\text{Pt}_{18.75}\text{Co}_{18.75}\text{Ta}_{12.5}$ ($\Delta H_f = -0.53$ eV/atom). It is interesting to notice that the quaternary substitution favours 6.25 at.% Ta and the structures become less stable with an increase in Ta addition above 6.25 at.%.

Table 8. Lattice parameters (Å) and heats of formation (eV/atom) for the B19 $\text{Ti}_{50}\text{Pt}_{43.75-x}\text{Co}_{6.25}\text{Ta}_x$ (6.25, 12.50 and 18.75 at.%) and $\text{Ti}_{50}\text{Pt}_{31.25-x}\text{Co}_{18.75}\text{Ta}_x$ (6.25 and 12.50 at.%) quaternary alloys.

Structures	Ti ₅₀ Pt _{43.75-x} Co _{6.25} Ta _x			Ti ₅₀ Pt _{31.25-x} Co _{18.75} Ta _x	
At.% Ta	6.25	12.50	18.75	6.25	12.50
<i>a</i>	2.20	2.24	2.21	4.41	4.39
<i>b</i>	3.13	3.13	3.26	2.96	3.14
<i>c</i>	4.58	4.58	4.40	2.30	2.20
ΔH _f	-0.75	-0.65	-0.55	-0.63	-0.53

6.2.2. Elastic constants for B19 TiPtCo-Ta

The elastic constants and moduli for the doped B19 $\text{Ti}_{50}\text{Pt}_{43.75-x}\text{Co}_{6.25}\text{Ta}_x$ and $\text{Ti}_{50}\text{Pt}_{31.25-x}\text{Co}_{18.75}\text{Ta}_x$ quaternary structures were determined as listed in Table 9. It is seen from Table 9 that the independent elastic constants are positive which results in positive shear modulus (C'). These findings suggest that all the quaternary alloys fulfil all conditions of stability of an orthorhombic crystal [3], therefore B19 $\text{Ti}_{50}\text{Pt}_{43.75-x}\text{Co}_{6.25}\text{Ta}_x$ and $\text{Ti}_{50}\text{Pt}_{31.25-x}\text{Co}_{18.75}\text{Ta}_x$ are considered to be mechanically stable. Anisotropy, A approaches unity (A

= 1) for all the systems which indicates a strong correlation between C_{44} and C' . This shows that the materials are elastically isotropic.

For $\text{Ti}_{50}\text{Pt}_{43.75-x}\text{Co}_{6.25}\text{Ta}_x$ alloys, $\text{Ti}_{50}\text{Pt}_{25}\text{Co}_{6.25}\text{Ta}_{18.75}$ (179.97 GPa) is resistant to compression since it has the highest bulk modulus and $\text{Ti}_{50}\text{Pt}_{31.25}\text{Co}_{6.25}\text{Ta}_{12.75}$ (179.22 GPa) has the lowest bulk modulus value. $\text{Ti}_{50}\text{Pt}_{18.75}\text{Co}_{18.75}\text{Ta}_{12.50}$ has the highest bulk modulus (173.29 GPa) hence it is more resistant to compression as compared to $\text{Ti}_{50}\text{Pt}_{25}\text{Co}_{18.75}\text{Ta}_{6.25}$ (83.27 GPa) for $\text{Ti}_{50}\text{Pt}_{31.25-x}\text{Co}_{18.75}\text{Ta}_x$ alloys. The calculated shear moduli (G) indicates that $\text{Ti}_{50}\text{Pt}_{31.25}\text{Co}_{6.25}\text{Ta}_{12.50}$ less rigid compared to the other concentration of Ta due to its low shear modulus for $\text{Ti}_{50}\text{Pt}_{43.75-x}\text{Co}_{6.25}\text{Ta}_x$ alloys. For $\text{Ti}_{50}\text{Pt}_{31.25-x}\text{Co}_{18.75}\text{Ta}_x$ alloys, the $\text{Ti}_{50}\text{Pt}_{18.75}\text{Co}_{18.75}\text{Ta}_{12.50}$ (53.21 GPa) is more rigid as compared to $\text{Ti}_{50}\text{Pt}_{25}\text{Co}_{18.75}\text{Ta}_{6.25}$ (13.62 GPa), the system becomes more rigid as Ta is increased above 6.25 at.%. Moreover, the calculated Young's (E) modulus suggest that $\text{Ti}_{50}\text{Pt}_{31.25}\text{Co}_{6.25}\text{Ta}_{12.50}$ and $\text{Ti}_{50}\text{Pt}_{25}\text{Co}_{18.75}\text{Ta}_{6.25}$ are elastic alloys as compared to other concentrations and this is due to their low Young's modulus for $\text{Ti}_{50}\text{Pt}_{43.75-x}\text{Co}_{6.25}\text{Ta}_x$ and $\text{Ti}_{50}\text{Pt}_{31.25-x}\text{Co}_{18.75}\text{Ta}_x$ alloys, respectively.

The Pugh's (B/G) ratio is calculated to further investigate the ductility and brittleness of the material. Interestingly, all the structures were found to be ductile since their Pugh's ratio is greater than the critical value (1.75) [142]. However, $\text{Ti}_{50}\text{Pt}_{31.25}\text{Co}_{6.25}\text{Ta}_{12.50}$ and $\text{Ti}_{50}\text{Pt}_{25}\text{Co}_{18.75}\text{Ta}_{6.25}$ are found to be the most ductile materials.

Table 9. Elastic properties, bulk, shear and Young's modulus (GPa) of the B19 TiPtCoTa quaternary alloys.

Structures	Ti ₅₀ Pt _{43.75-x} Co _{6.25} Ta _x			Ti ₅₀ Pt _{31.25-x} Co _{18.75} Ta _x	
At.% Ta	Ta _{6.25}	Ta _{12.50}	Ta _{18.75}	Ta _{6.25}	Ta _{12.50}
C ₁₁	280.21	266.47	281.70	223.41	237.68
C ₁₂	154.12	150.02	124.58	154.03	131.44
C ₁₃	135.88	149.96	145.38	128.41	150.41
C ₂₂	250.63	258.89	252.95	141.11	259.71
C ₂₃	137.63	142.26	142.52	161.84	130.78
C ₃₃	235.86	214.41	260.10	227.85	237.00
C ₄₄	42.09	42.90	55.98	18.11	51.79
C ₅₅	50.98	41.73	70.45	24.75	50.70
C ₆₆	64.30	57.17	52.70	43.77	58.60
C'	63.05	58.23	78.56	34.69	53.12
A ₁	1.02	0.98	0.67	1.26	1.10
A ₂	0.35	0.47	0.45	0.19	0.60
A ₃	0.65	0.75	1.06	0.41	0.88
B	179.37	179.22	179.97	83.27	173.29
G	53.43	47.64	60.77	13.62	53.21
E	145.81	131.28	260.74	38.73	144.81
B/G	3.36	3.76	2.96	6.11	3.26

6.2.3. Phonon dispersion curves for B19 TiPtCo-Ta

Figure 40 shows the phonon dispersion and phonon DOS for the B19 Ti₅₀Pt_{37.50}Co_{6.25}Ta_{6.25} structure. The phonon spectra for Ti₅₀Pt_{37.50}Co_{6.25}Ta_{6.25} does not show any soft modes implying that the system is vibrationally stable as shown in Figure 40 (a). There are imaginary modes observed along the gamma and X high symmetry directions, this is due to the moderate contribution of Pt z-axis in the negative frequency as shown in Figure 40 (b). The phonon DOS indicates that there is a negligible vibration

in the negative frequency which results in the stability of the structure. The phonon modes found below 6 THz are due to Pt, Co and Ta atoms while above 6 THz is due to Ti atoms. These results are consistent with the calculated elastic constants.

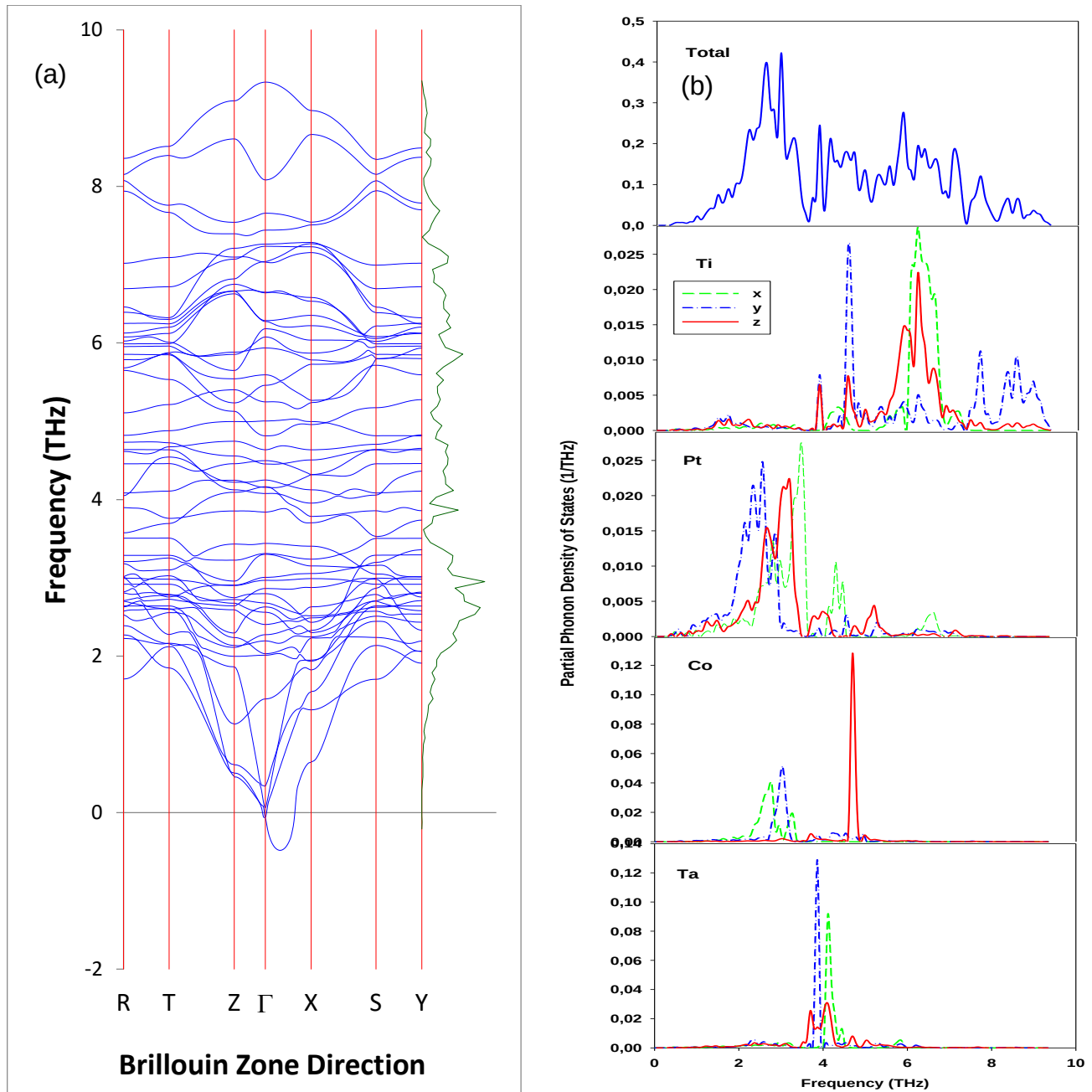


Figure 40. Phonon dispersion curves (a) and phonon DOS (b) for B19

Ti₅₀Pt_{37.50}Co_{6.25}Ta_{6.25}.

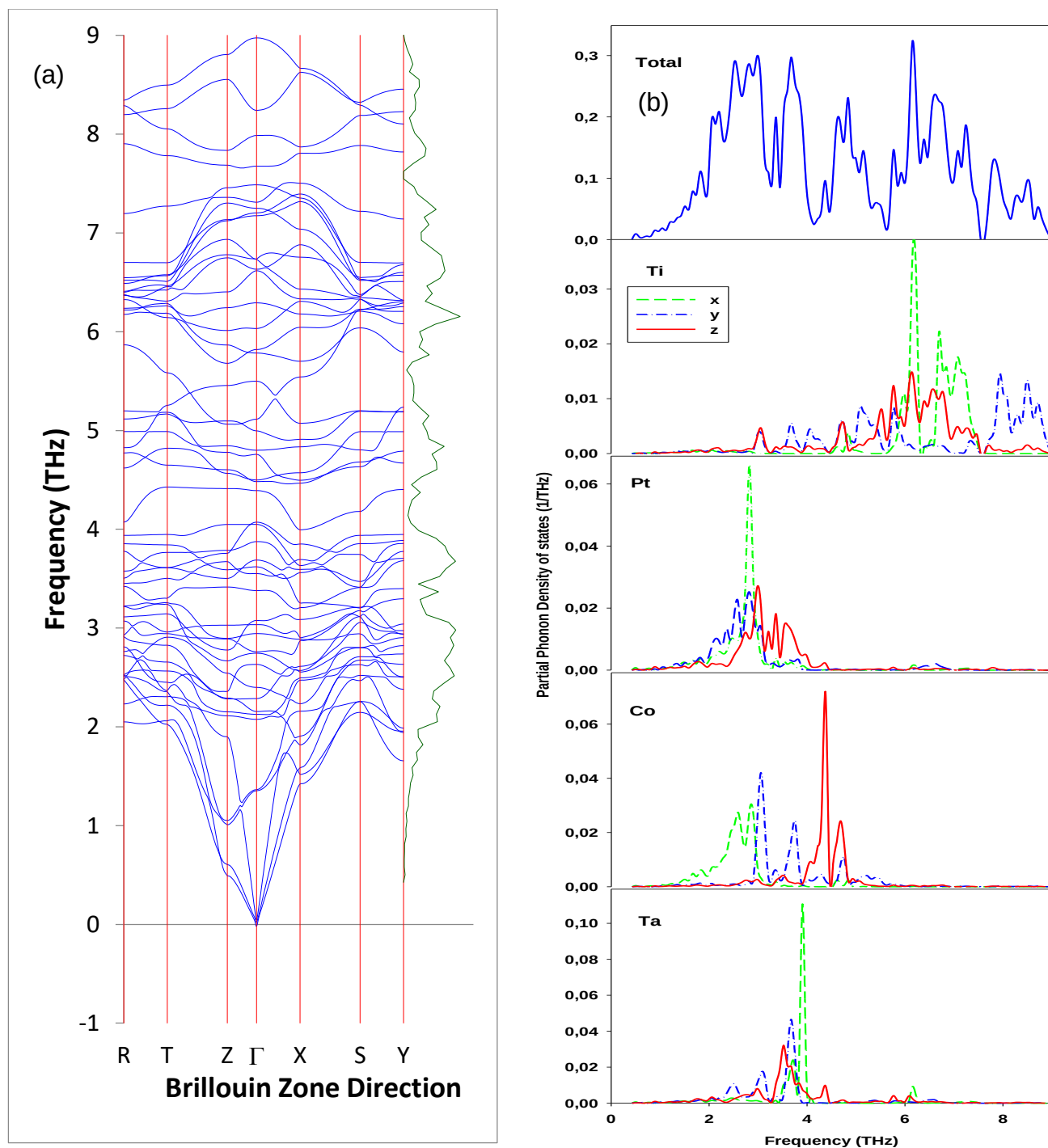


Figure 41. Phonon dispersion curves (a) and phonon DOS (b) for B19

$\text{Ti}_{50}\text{Pt}_{31.25}\text{Co}_{6.25}\text{Ta}_{12.50}$.

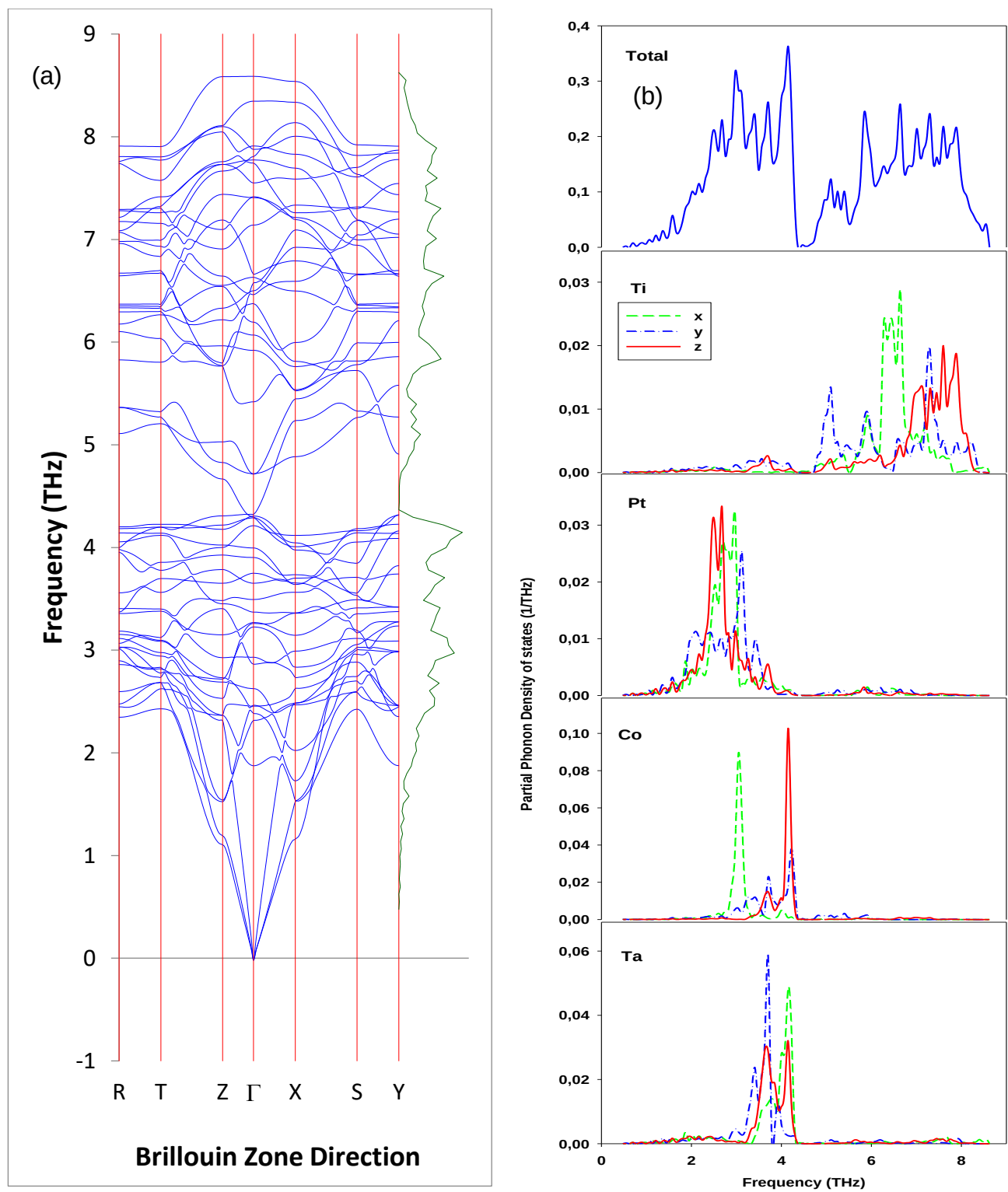


Figure 42. Phonon dispersion curves (a) and phonon DOS (b) for B19

$\text{Ti}_{50}\text{Pt}_{25}\text{Co}_{6.25}\text{Ta}_{18.75}$.

Figures 41 and 42 show the phonon dispersion curves and phonon DOS for $\text{Ti}_{50}\text{Pt}_{31.25}\text{Co}_{6.25}\text{Ta}_{12.50}$ and $\text{Ti}_{50}\text{Pt}_{25}\text{Co}_{6.25}\text{Ta}_{18.75}$, respectively. The absence of soft modes or lack of vibration in the negative frequency on the phonon dispersion curves shows that both structures are the vibrational stable. Phonon modes observed below 5 THz are due to Pt, Co and Ta atoms contributions while above 5 THz they are due to Ti atoms (in Figure 41 (b)). The phonon dispersion curves show that as the Ta content increases, the structure becomes more vibrational stable. This indicates that Ta plays an important role in the vibrational stability of TiPtCo ternaries.

Phonon dispersion curves of B19 $\text{Ti}_{50}\text{Pt}_{25}\text{Co}_{18.75}\text{Ta}_{6.25}$ and $\text{Ti}_{50}\text{Pt}_{18.75}\text{Co}_{18.75}\text{Ta}_{12.50}$ alloys are shown in Figures 43 and 44, respectively. In Figure 43 (a), there are soft modes observed in the high symmetry direction which allude to the instability of the structure. This is deduced from all phonon branches lying below 0 THz. This is an indication that $\text{Ti}_{50}\text{Pt}_{25}\text{Co}_{18.75}\text{Ta}_{6.25}$ phase is unstable. The partial phonon DOS display that the soft modes are due to the vibration of Co and Pt atoms as shown in Figure 43 (b). The vibrations are observed at a frequency of approximately -2 THz. The soft modes observed are along with R, T, Z, X, S, Y and Γ directions on the phonon spectra. Moreover, the results show that as the concentration of Ta is increased to 12.50 at.%, the structure becomes vibrationally stable. In Figure 44 (a), it is seen that there are no soft modes observed, which indicates the stability of the structure at the high content of Ta. The partial phonon DOS display that the absence of soft modes is due to the vibration of atoms above 0 THz as shown in Figure 44 (b).

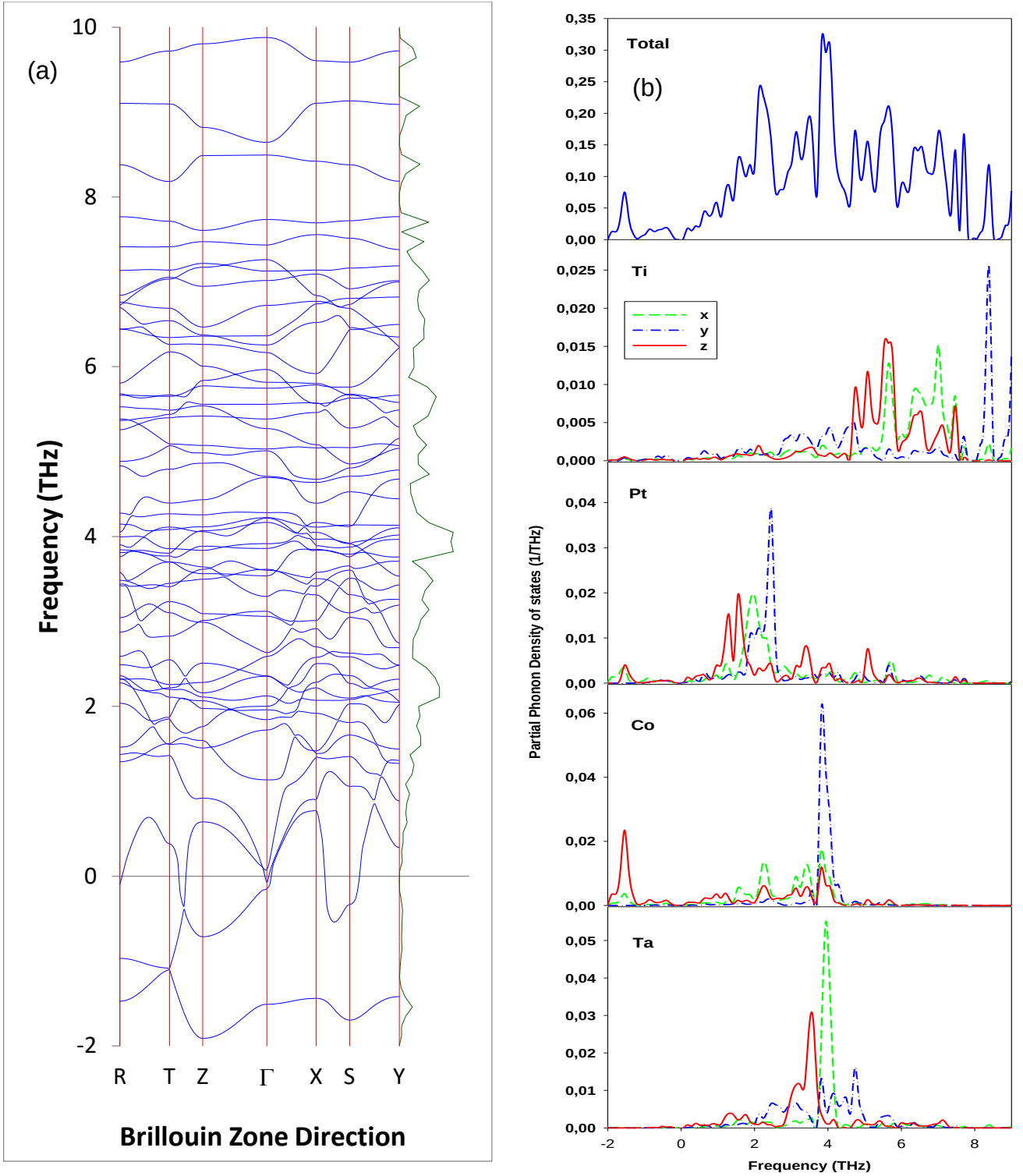


Figure 43. Phonon dispersion curves (a) and phonon DOS (b) for B19

$\text{Ti}_{50}\text{Pt}_{25}\text{Co}_{18.75}\text{Ta}_{6.25}$.

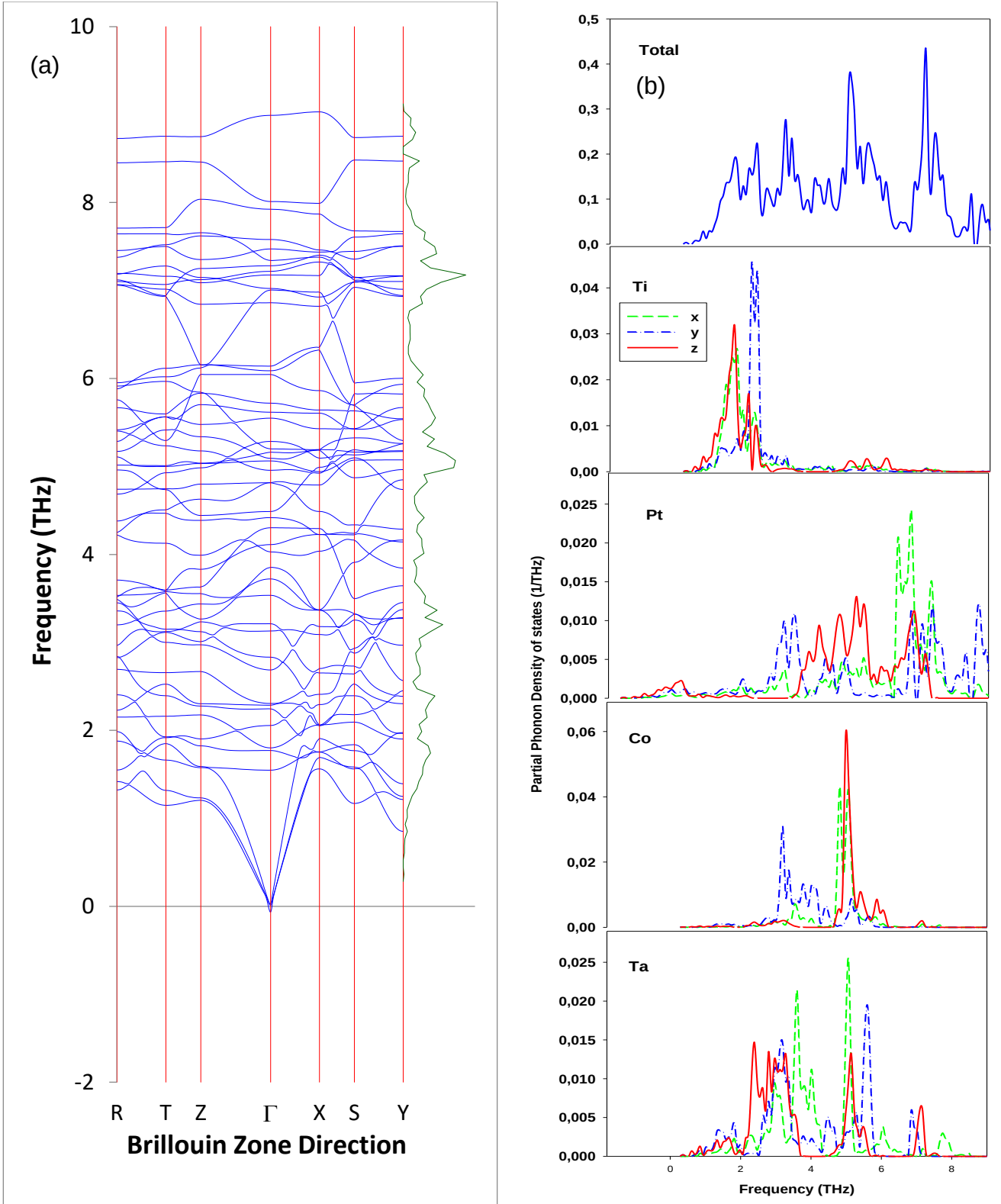


Figure 44. Phonon dispersion curves (a) and phonon DOS (b) for B19

$\text{Ti}_{50}\text{Pt}_{18.75}\text{Co}_{18.75}\text{Ta}_{12.50}$.

6.2.4. Density of states for B19 TiPtCo-Ta

In Figure 45, the density of states for the $\text{Ti}_{50}\text{Pt}_{37.50}\text{Co}_{6.25}\text{Ta}_{6.25}$ and $\text{Ti}_{50}\text{Pt}_{31.25}\text{Co}_{6.25}\text{Ta}_{12.50}$ and their partial DOS are shown. Figure 45 (a) shows the density of states (DOS) and partial density of states (PDOS) of B19 $\text{Ti}_{50}\text{Pt}_{37.50}\text{Co}_{6.25}\text{Ta}_{6.25}$ to deduce its stability. We observe a dominant peak in the valence band at approximately -5 eV which is attributed to Pt d-states. We note that Pt, Co and Ta d-states are dominant at about -5, -3 and -1 eV, respectively. Moreover, DOS at the Fermi level is characterized by a peak which is Ti d-states contribution. Moreover, we observe a small peak in the conduction band which is a contribution of mainly Ti d-states.

In Figure 45 (b), the DOS and PDOS of B19 $\text{Ti}_{50}\text{Pt}_{31.25}\text{Co}_{6.25}\text{Ta}_{12.50}$ are shown. There is a high contribution of Pt d-states towards the dominant peak observed at about -5 eV and less of Ti, Co and Ta d-states. It is noted that an increase in Ta content from 6.25 to 12.50 at.% increases the dominant peak. The peak at -2 eV is dominated by Co d-states contribution and at -1 eV with Ta d-states contribution. Both peaks increase with an increase in Ta composition. The peak at the Fermi level shift towards the conduction band, and it is attributed to Ti d-states contribution. Moreover, there is a contribution of Ti d-states towards the conduction band.

The TDOS and PDOS of the B19 $\text{Ti}_{50}\text{Pt}_{25}\text{Co}_{6.25}\text{Ta}_{18.75}$ alloys are shown in Figure 46. We observe a shift of peaks towards the valence band with the addition of 18.75 at.% Ta to the system. All the peaks are in the valence band. The dominant peak is observed at about -3 eV and is attributed to contribution mainly of Co d-states. There is a shift of peak observed from -5 eV to -6 eV and the peak is a contribution of Pt, Ti and Ta d-states. There are no peaks observed towards the Fermi level and the conduction band.

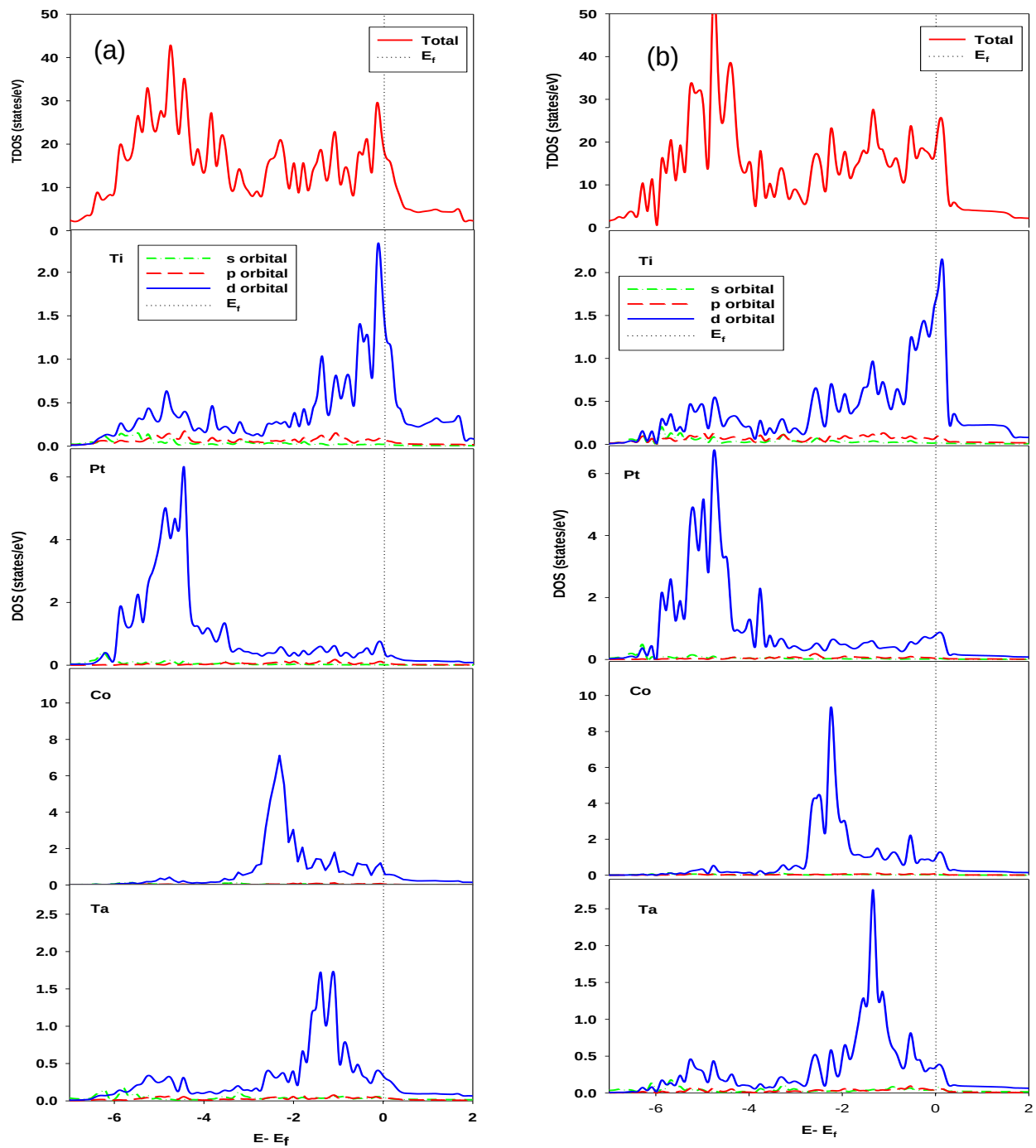


Figure 45. Total and partial density of states for the B19 (a) $\text{Ti}_{50}\text{Pt}_{37.50}\text{Co}_{6.25}\text{Ta}_{6.25}$ and (b) $\text{Ti}_{50}\text{Pt}_{31.25}\text{Co}_{6.25}\text{Ta}_{12.50}$.

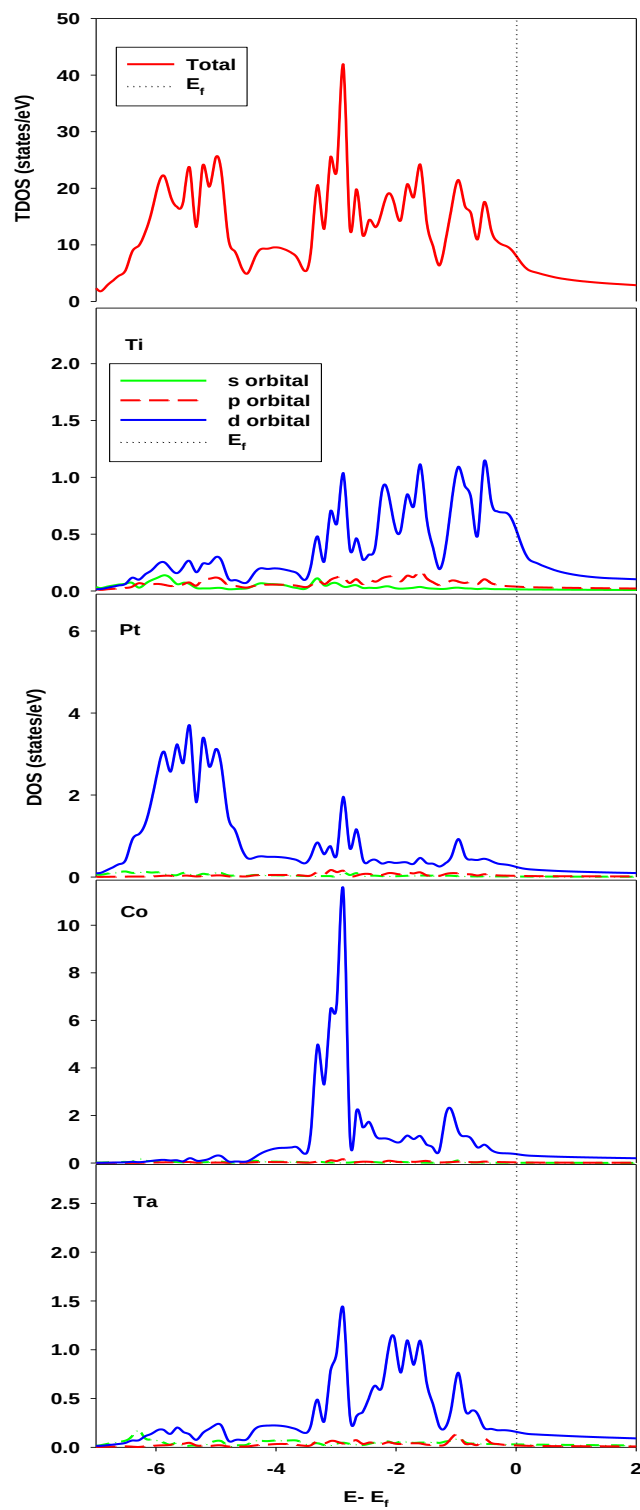


Figure 46. Total and partial density of states for the B19 $\text{Ti}_{50}\text{Pt}_{25}\text{Co}_{6.25}\text{Ta}_{18.75}$.

The total and partial DOS of B19 $\text{Ti}_{50}\text{Pt}_{25}\text{Pt}_{18.75}\text{Ta}_{6.25}$ is shown in Figure 47 (a). We observe more peaks in the valence band as compared to the conduction band. The dominant peak is observed at about -5 eV, which is attributed to Pt d-states. There is a less contribution of Ti and Ta d-states observed towards the dominant peak. There is a high contribution of Co d-states towards the peak observed at approximately -1.5 eV. The Fermi level coincides with a small peak, which is characterized by Ti, Co and Ta d-states. The peak at about -1 eV is dominated by Ta d-states. Moreover, there are peaks observed in the conduction band which are due to Ti d-states contribution.

Figure 47 (b) shows the total and PDOS of $\text{Ti}_{50}\text{Pt}_{18.75}\text{Co}_{18.75}\text{Ta}_{12.50}$. The dominant peak is now observed at -2 eV attributed to Co d-states. We note that the peak observed at -5 eV decreases as Ta content increase in the system. The peak at -1.5 eV shift to -2 eV and peak at -1 eV decrease attributed to Ta d-states. Increase in Ta content increases the Co d-states peak observed at -2 eV. Moreover, we observe a peak at the Fermi level which is the contribution mainly from Ti d-states and peaks observed in the conduction band decreases.

Figures 48 and 49, show the total DOS of the B19 $\text{Ti}_{50}\text{Pt}_{43.75-x}\text{Co}_{6.25}\text{Ta}_x$ ($x = 6.25, 12.50$ and 18.75 at.%) and $\text{Ti}_{50}\text{Pt}_{31.25-x}\text{Co}_{18.75}\text{Ta}_x$ ($x = 6.25$ and 12.50 at.%) quaternary alloys, respectively. In Figure 48, it is seen that $\text{Ti}_{50}\text{Pt}_{37.50}\text{Co}_{6.25}\text{Ta}_{6.25}$ has a lower number of DOS at the Fermi level as compared to $\text{Ti}_{50}\text{Pt}_{31.25}\text{Co}_{6.25}\text{Ta}_{12.50}$, which suggest that 6.25 at.% Ta is more favourable (stable). We observe that with the addition of 18.75 at.% Ta the peaks shift towards the valence band which suggest the reduced stability at this composition. Moreover, it is noted that $\text{Ti}_{50}\text{Pt}_{25}\text{Co}_{18.75}\text{Ta}_{6.25}$ is the most stable quaternary alloy as compared to $\text{Ti}_{50}\text{Pt}_{18.75}\text{Co}_{18.75}\text{Ta}_{12.50}$ as shown in Figure 49. This is due to the lower

number of DOS at the Fermi level. These results are in good agreement with the predicted heats of formation.

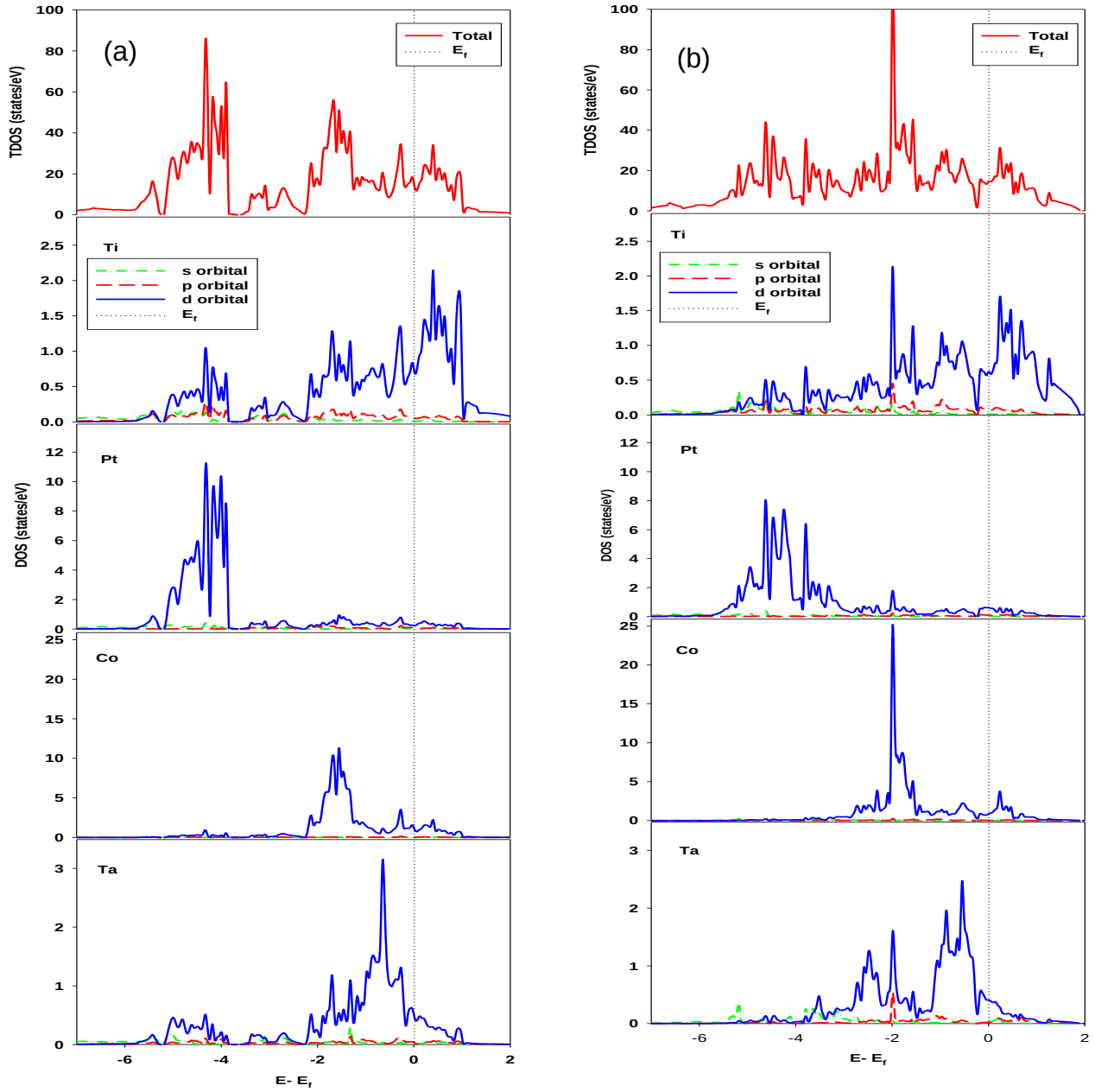


Figure 47. Total and partial density of states for the B19 (a) $\text{Ti}_{50}\text{Pt}_{25}\text{Co}_{18.75}\text{Ta}_{6.25}$ and (b) $\text{Ti}_{50}\text{Pt}_{18.75}\text{Co}_{18.75}\text{Ta}_{12.50}$.

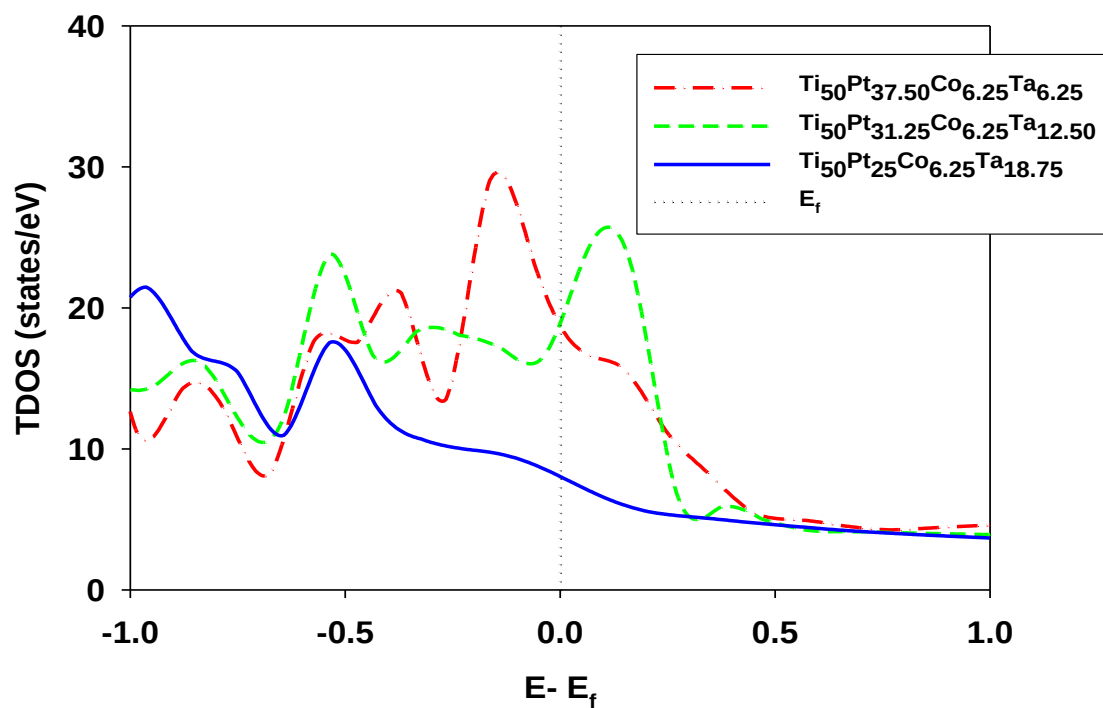


Figure 48. Total density of states for B19 $\text{Ti}_{50}\text{Pt}_{43.75-x}\text{Co}_{6.25}\text{Ta}_x$ alloys.

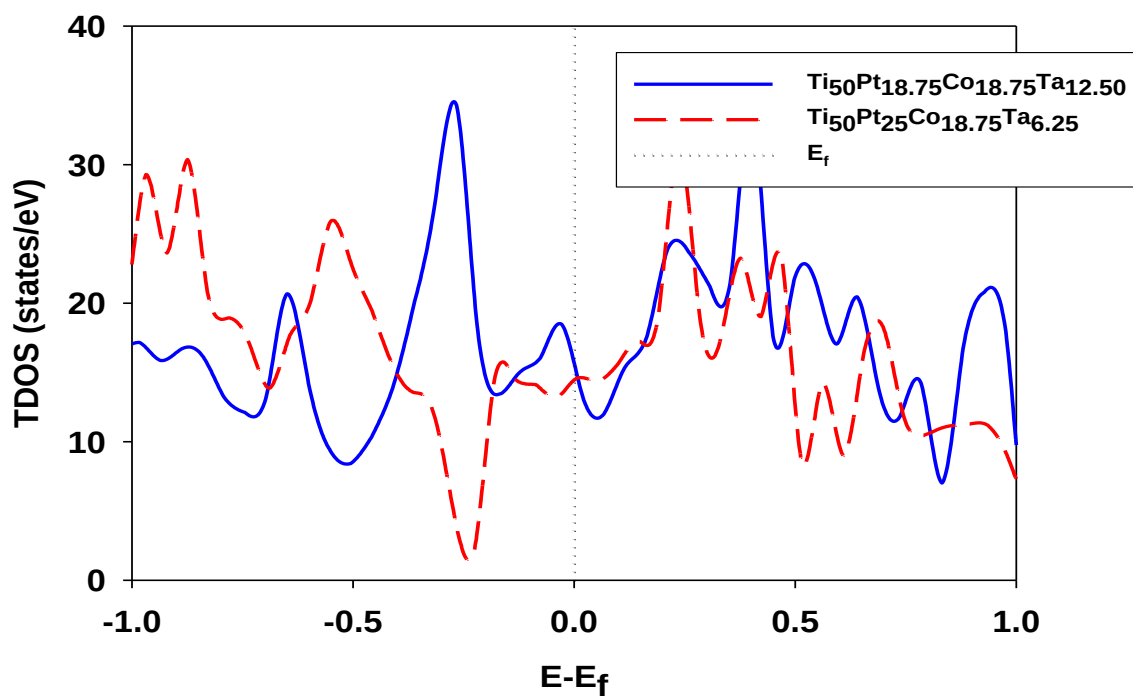


Figure 49. Total density of states of B19 $\text{Ti}_{50}\text{Pt}_{31.25-x}\text{Co}_{18.75}\text{Ta}_x$ alloys.

6.3. Temperature Dependence: B19 TiPtCo-Ta

In this section, the effect of temperature on lattice parameters and X-ray diffraction for the B19 $\text{Ti}_{50}\text{Pt}_{37.50}\text{Co}_{6.25}\text{Ta}_{6.25}$ and $\text{Ti}_{50}\text{Pt}_{25}\text{Co}_{18.75}\text{Ta}_{6.25}$ is investigated. The investigated structures were deduced in Section 6.2 (Table 8) where they were found to be the most stable with respect to their heats of formations. LAMMPS code [127] which employs the embedded atom method (EAM) [144] where the Zhou [145] interatomic potentials were invoked was used to investigate the temperature dependence of these alloys. A 10x10x10 supercell with 1024 atoms was generated for both the structures and the temperature was varied from 100 to 1800 K. The study will give insights on the possible transformation that may occur between the orthorhombic B19, also known as the martensite phase, and the cubic B2 phase referred to as the austenite phase.

6.3.1. Lattice expansion of B19 TiPtCo-Ta alloys

In Figures 50, the graph of temperature against the lattice parameters of the B19 $\text{Ti}_{50}\text{Pt}_{37.50}\text{Co}_{6.25}\text{Ta}_{6.25}$ is shown. The a and c lattice parameters for the $\text{Ti}_{50}\text{Pt}_{37.50}\text{Co}_{6.25}\text{Ta}_{6.25}$ structure increases minimally with temperature. Interestingly, as the temperature is increased, the lattice parameters collapse at approximately 400 K. At temperatures above 400 K, there is a slight sharp increase and the lattice parameters start to be almost constant till 1700 K where the structure starts to melt. The b lattice parameter increases linearly with an increase in temperature and a drastic increase is observed at about 400 K. However, there is a minimal increase of all the lattice parameters with temperature from 600 to 1650 K. At temperatures above 1650 K, the a and b parameters significantly increase whilst the c lattice parameter collapses. At these temperatures, the structure has melted.

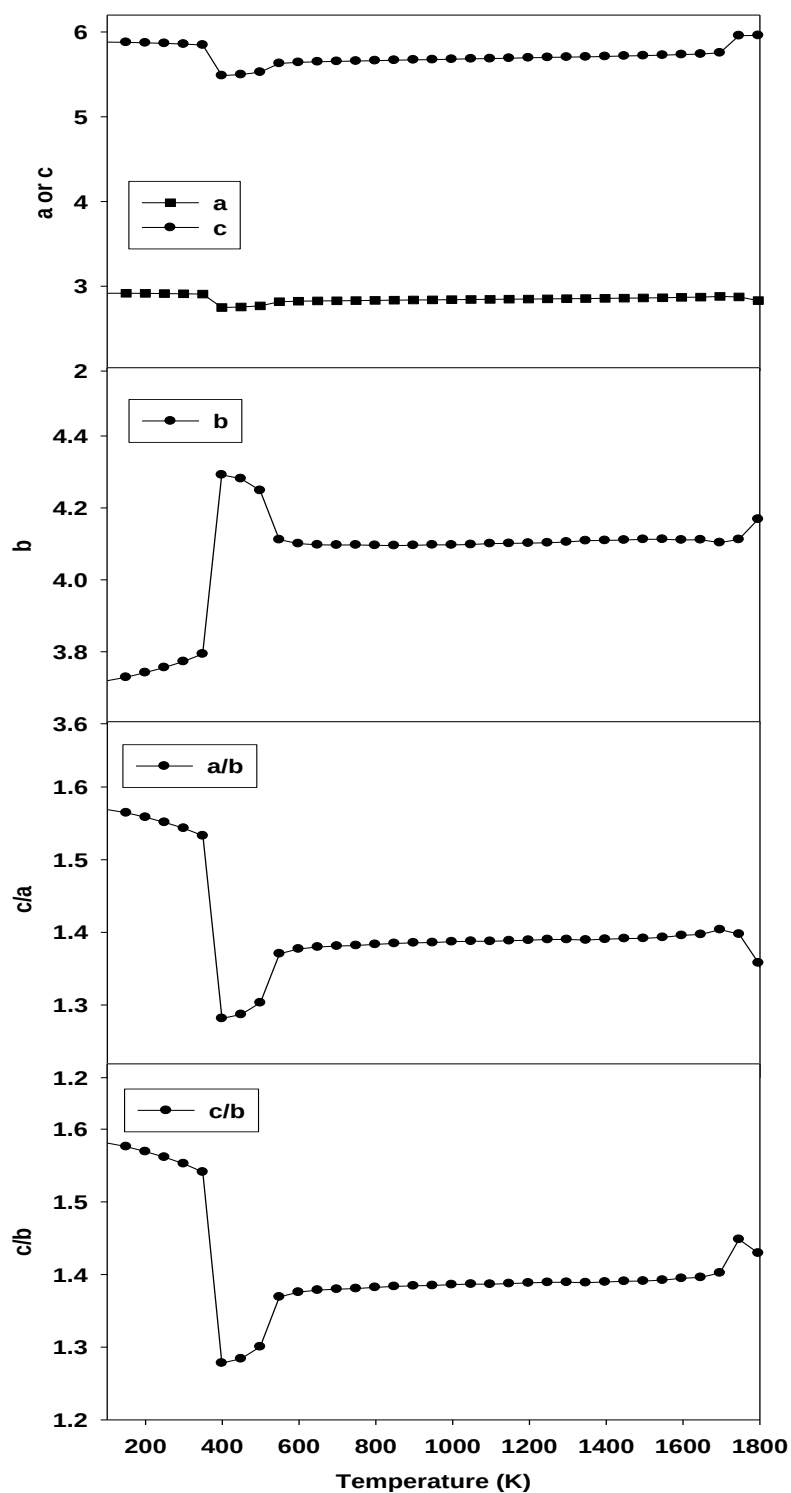


Figure 50. The temperature effect on lattice parameter and lattice ratio a/b or c/b of B19 at varied temperature for $\text{Ti}_{50}\text{Pt}_{37.50}\text{Co}_{6.25}\text{Ta}_{6.25}$.

In addition, the a/b and c/b ratios of the B19 $\text{Ti}_{50}\text{Pt}_{37.50}\text{Co}_{6.25}\text{Ta}_{6.25}$ were calculated as shown in Figure 50. The plots decrease linearly with an increase in temperature and a similar trend was observed experimentally for B19 TiPt [16]. Mitarai et al suggested that for the orthorhombic B19 to cubic B2 transformation to occur, c/b should be close to 1.414 with an increase in temperature [16]. In Figure 50, c/b ratio of the B19 $\text{Ti}_{50}\text{Pt}_{37.50}\text{Co}_{6.25}\text{Ta}_{6.25}$ is 1.369 and 1.402 at approximately 550 and 1700 K, respectively. The percentage difference of the anticipated ratio is within 0.85 % which may suggest that between the temperatures of 550 and 1700 K the B19 phase has transformed to the cubic B2 phase. The same behaviour is noted with c/b ratio wherein the structure melts at temperatures above 1700 K. The temperature at which the transformation takes place is lower than that of the pure B19 which suggest that Ta content addition reduces the transformation temperature of the system of TiPt [16] and TiPtCo [53, 17].

In Figure 51, the temperature dependence of the lattice parameter for $\text{Ti}_{50}\text{Pt}_{25}\text{Co}_{18.75}\text{Ta}_{6.25}$ is shown. The a parameter increases from 100 K to 600 K where the decrease is observed. Moreover, the a parameter increases at temperatures above 600 K and at 1700 K the structure loses its shape which suggests melting. The c parameter increases with temperature from 100 K to 600 K. We note that the c parameter decreases at 600 K and increases at temperatures above 600 K. The b parameter increases with temperature from 100 K to 600 K where we observe a rapid rise. It is observed that above 750 K, the lattice parameter increases with temperature and at around 1700 K the drop in the plot is observed.

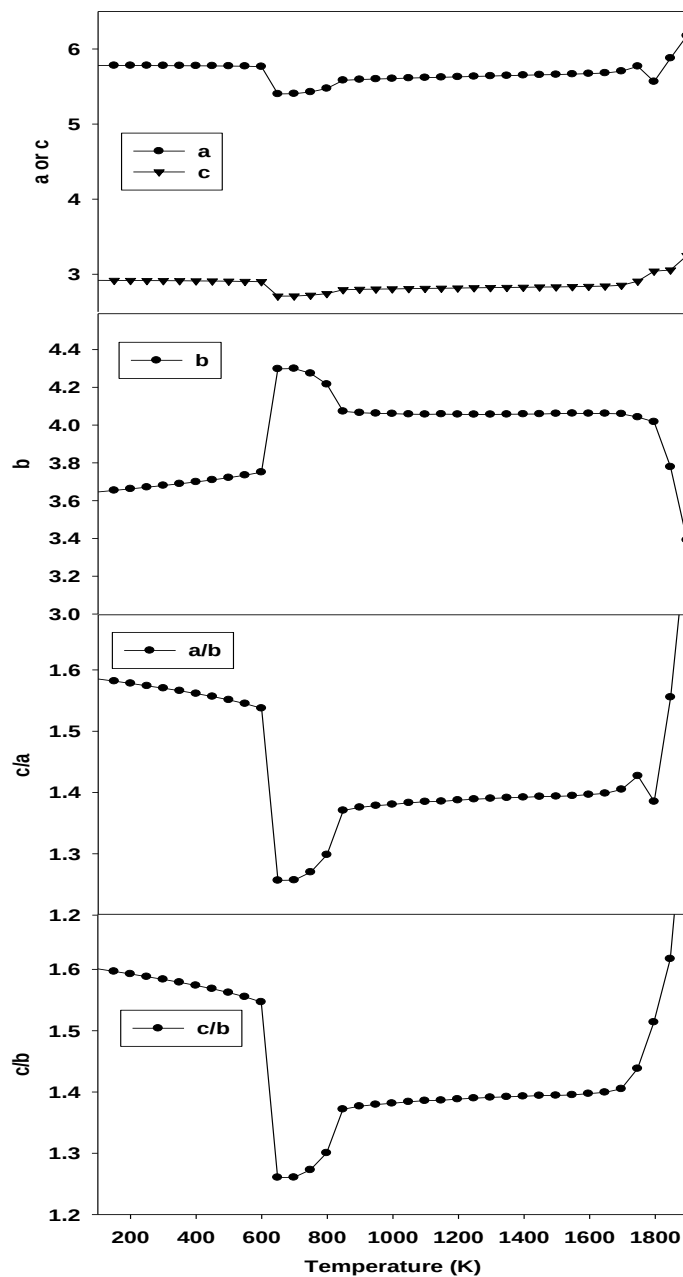


Figure 51. The temperature effect on lattice parameter and lattice ratio a/b or c/b of B19 at varied temperature for $\text{Ti}_{50}\text{Pt}_{25}\text{Co}_{18.75}\text{Ta}_{6.25}$.

The ratio a/b and c/b of $\text{Ti}_{50}\text{Pt}_{25}\text{Co}_{18.75}\text{Ta}_{6.25}$ has a value of 1.537 and 1.560 at approximately 600 K, respectively. At 650 K, c/b ratio is found to be 1.261 which suggest that at this temperature the B19 structure is transforming to B2 phase. Moreover, c/b ratio increases with an increase in temperature and at 850 K the ratio is approximately 1.372

and 1.400 at 1600 K. The temperature at which the transformation happens for both $\text{Ti}_{50}\text{Pt}_{37.50}\text{Co}_{6.25}\text{Ta}_{6.25}$ and $\text{Ti}_{50}\text{Pt}_{25}\text{Co}_{18.75}\text{Ta}_{6.25}$ is lower compared to TiPt [16] and for ternary $\text{Ti}_{50}\text{Pt}_{50-x}\text{Co}_x$ ($x = 6.25, 18.75$ and 25) [53]. The transformation temperature for binary TiPt is about 1300 K [16] while for ternary TiPtCo is 1203 K [22]. The trend of lattice parameters is similar and comparable with the previous experimental [16] and theoretical findings [146]. The structure has melted at temperatures above 1750 K.

6.3.2. X-ray diffraction of B19 TiPtCo-Ta alloys

X-ray powder diffraction (XRD) is a rapid analytical method which exhibits statistics about the crystal structure, chemical composition, and physical properties of the material [147]. These techniques are used for the phase identification of many systems like quaternary alloys at varied temperature. The XRD patterns of the shape memory alloys have been reported experimentally where the transition from B19 to B2 $\text{Ti}_{50}\text{Pt}_{50}$ has been observed [16, 43]. In this study, the XRD analysis of the B19 TiPtCoTa for both austenite and martensite phases were performed from ambient to high temperatures and compared with the available experiments.

Figure 52 shows the simulated B19 $\text{Ti}_{50}\text{Pt}_{37.50}\text{Co}_{6.25}\text{Ta}_{6.25}$ X-ray diffraction patterns from a 100 to 1800 K. We observe many peaks at 100 K, which show a B19 pattern up to 400 K with dominant peak [011]. As the temperature increases, the number of peaks reduces at 400 K where there is a shift of [101] peak. Moreover, we note a shift of [002], [101] and [200] peaks at 500 K which suggest the phase change into B2 patterns. Moreover, as the temperature increases to 1700 K the [100] peak decreases which suggest the melting of the structure. B2 phase is observed from 500 to 1700 K and at 1800 K the

structure loses its shape where melting is observed. The results are in good agreement with our predicted lattice expansion which suggests early transformation.

In Figures 53, the XRD patterns of the $\text{Ti}_{50}\text{Pt}_{25}\text{Co}_{18.75}\text{Ta}_{6.25}$ are shown. The peaks at 100 K, show the B19 pattern. The dominant [011] peak is observed at $40^\circ 2\theta$ from 100 to 900 K. As the temperature increases from 100 K, the number of peaks reduces. At 900 K, we observe a shift of [011] peak and also split into two peaks which suggest a phase change at this temperature. We observe a reduced number of peaks from 900 K to 1600 K. Moreover, B2 patterns are observed from 900 to 1600 K and at 1700 K the structure loses its shape where melting is observed. These XRD findings are in good agreement with our predicted lattice expansion transformation temperatures.

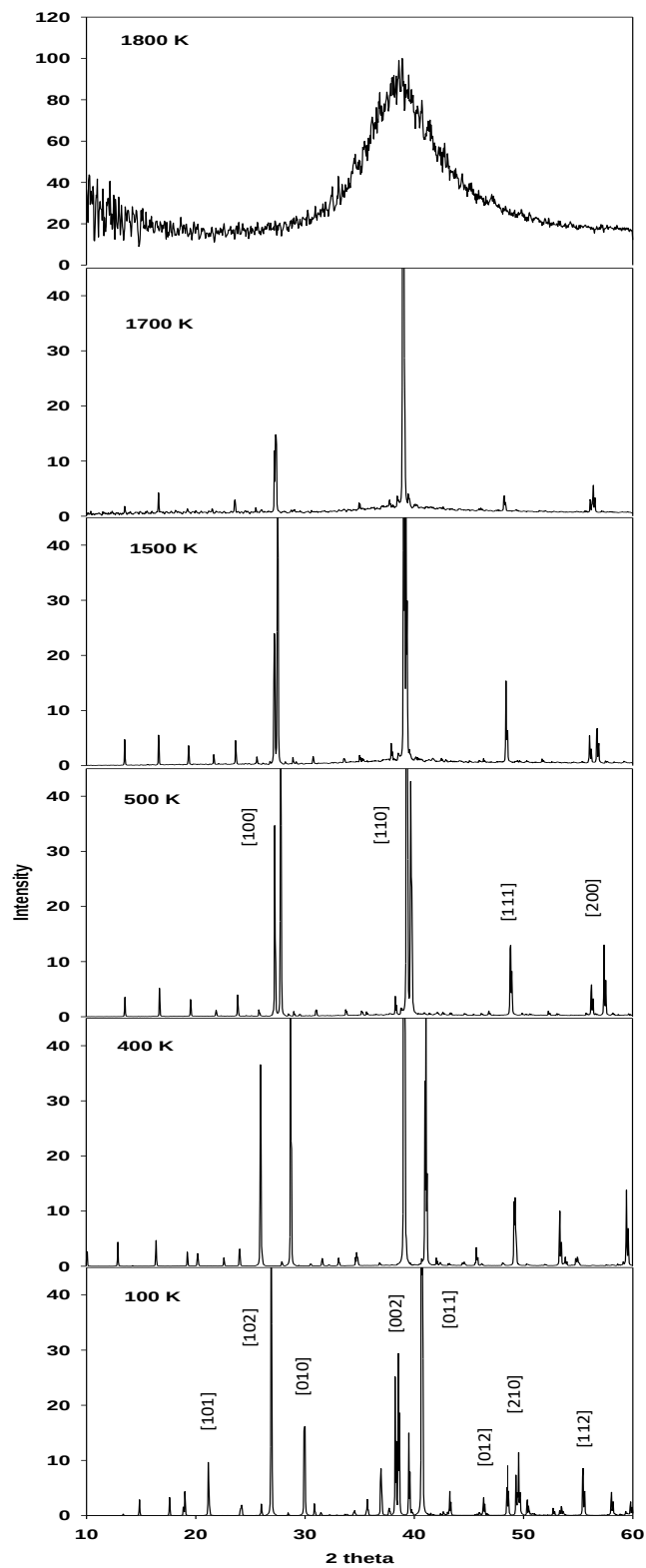


Figure 52. The simulated B19 $\text{Ti}_{50}\text{Pt}_{37.5}\text{Co}_{6.25}\text{Ta}_{6.25}$ X-ray diffraction patterns from 100 to 1800 K.

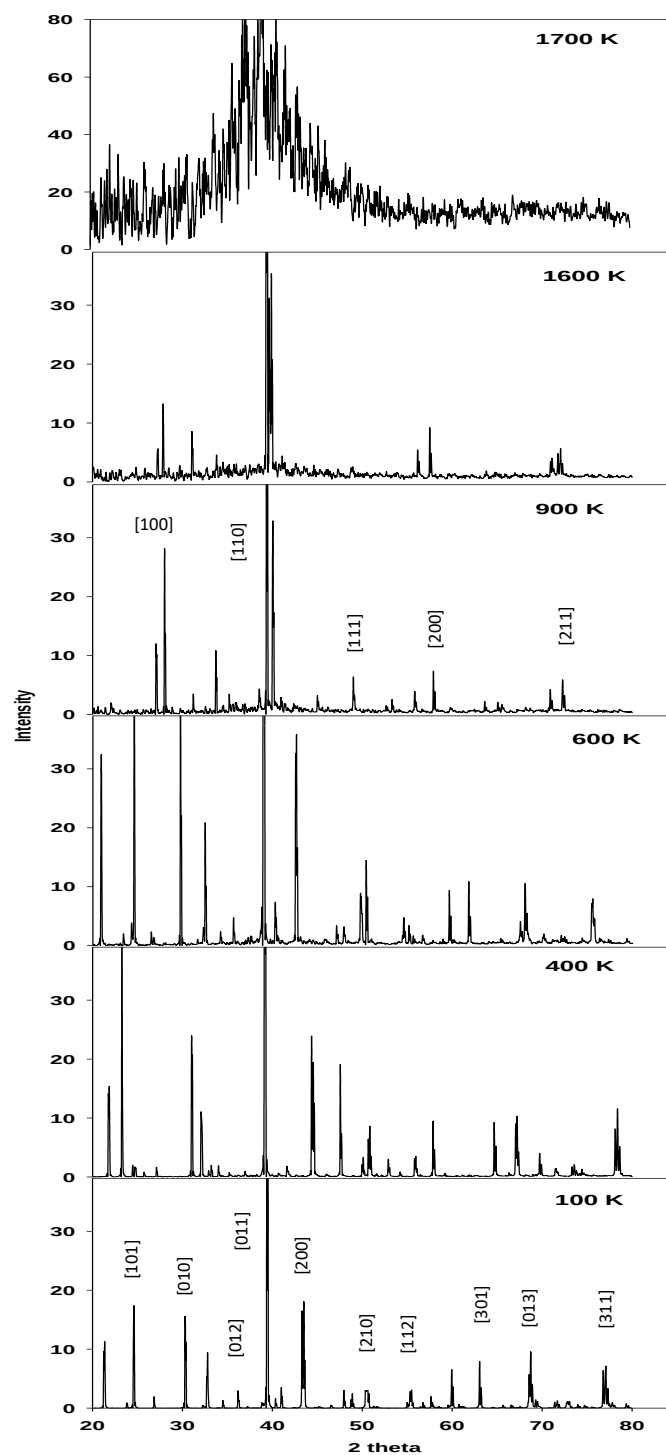


Figure 53. The simulated B19 $\text{Ti}_{50}\text{Pt}_{25}\text{Co}_{18.75}\text{Ta}_{6.25}$ X-ray diffraction patterns from 100 to 1700 K.

6.4. Summary

In summary, for $\text{Ti}_{50}\text{Pt}_{43.75-x}\text{Co}_{6.25}\text{Ta}_x$ alloys, the predicted heats of formation on the B2 structures favour the 6.25 at.% Ta. The DOS confirmed the predicted stability of the alloys as predicted by ΔH_f . For $\text{Ti}_{50}\text{Pt}_{31.25-x}\text{Co}_{18.75}\text{Ta}_x$ alloys, 6.25 at.% Ta is more favourable since it has the lower heats of formation value. Moreover, DOS show that 12.50 at.% Ta is most favourable, which is inconsistent with predicted heats of formation. All the quaternary alloys were found to be mechanical stable since their C_{ij} 's satisfy the cubic stability criteria. Moreover, 6.25 and 18.75 at.% Ta is found to be ductile ($B/G > 1.75$). It was also found that the 6.25 at.% Ta was vibrationally unstable whereas 18.75 at.% Ta was stable with no soft modes observed in the negative frequency region of the phonon curve. Furthermore, the structure was found to be mechanically stable and becomes vibrational stable as Ta content is increased to 12.50 at.%.

Furthermore, the ab initio calculations on the B19 $\text{Ti}_{50}\text{Pt}_{43.75-x}\text{Co}_{6.25}\text{Ta}_x$ and $\text{Ti}_{50}\text{Pt}_{31.25-x}\text{Co}_{18.75}\text{Ta}_x$ were conducted. The predicted heats of formation favoured the 6.25 at.% Ta for both $\text{Ti}_{50}\text{Pt}_{43.75-x}\text{Co}_{6.25}\text{Ta}_x$ and $\text{Ti}_{50}\text{Pt}_{31.25-x}\text{Co}_{18.75}\text{Ta}_x$ alloys. Elastic properties were determined and all the C_{ij} 's show that both $\text{Ti}_{50}\text{Pt}_{43.75-x}\text{Co}_{6.25}\text{Ta}_x$ and $\text{Ti}_{50}\text{Pt}_{31.25-x}\text{Co}_{18.75}\text{Ta}_x$ are mechanically stable, anisotropic and are ductile. The $\text{Ti}_{50}\text{Pt}_{43.75-x}\text{Co}_{6.25}\text{Ta}_x$ system is vibrationally stable which is consistent with the predicted elastic constants. Similarly, $\text{Ti}_{50}\text{Pt}_{31.25-x}\text{Co}_{18.75}\text{Ta}_x$ becomes vibrationally stable as the Ta content increases. From DOS, we note that the 6.25 at.% Ta composition is favourable for both $\text{Ti}_{50}\text{Pt}_{43.75-x}\text{Co}_{6.25}\text{Ta}_x$ and $\text{Ti}_{50}\text{Pt}_{31.25-x}\text{Co}_{18.75}\text{Ta}_x$ alloys.

The predicted transformation temperature for $\text{Ti}_{50}\text{Pt}_{37.50}\text{Co}_{6.25}\text{Ta}_{6.25}$ is 500 K. The temperature predictions may suggest regions where possible martensitic transformations

are likely to occur and were confirmed from the structural patterns using the X-ray diffraction (XRD). This may imply that the $\text{Ti}_{50}\text{Pt}_{43.75-x}\text{Co}_{6.25}\text{Ta}_x$ has potential for HTSMA applications. Moreover, the predicted transformation temperature for $\text{Ti}_{50}\text{Pt}_{25}\text{Co}_{18.75}\text{Ta}_{6.25}$ is 600 K. The XRD patterns confirms the transformation temperature predictions. It was observed that the transformation temperature of TiPtCo reduces with the addition of Ta.

CHAPTER 7

SUMMARY AND CONCLUSION

We have studied the relative stability of binary Ti-based systems, the effect of alloying for binary and quaternary alloy systems, using the density functional approach. In chapter 4, the equilibrium lattice parameters of the TiPt, TiNi, TiCo and TiTa were calculated and are in good agreement with the experimental findings. Moreover, B2 TiPt was found to be the most stable alloy suggested by low heats of formation whereas TiTa is thermodynamically unstable due to high heats of formation value. In addition, the DOS confirmed the thermodynamic stability of the binary structures content within the predicted heats of formation trend. Elastic properties of TiNi, TiCo and TiTa suggest that the structures are mechanically stable due to positive C_{ij} 's values satisfy the cubic stability conditions. However, TiPt was found to be mechanically unstable due to the negative shear modulus ($C' < 0$). The phonon dispersion results confirmed the instabilities of TiPt due to the existence of negative vibrations along high symmetry direction of the Bz. Ternary addition on the B2 TiPt alloy has been suggested to enhance the stability and mechanical properties of the structure.

In Chapter 5, the first principle study on the effect of V, Ta and Hf alloying elements on the B2 TiPt binary alloy was conducted. The equilibrium lattice parameters of TiPtM were found to be decreasing with an increase in V while increases with an increase in Ta and Hf content. The heats of formations proposed that the systems are stable with low negative values ($\Delta H_f < 0$). $\text{Ti}_{50}\text{Pt}_{43.75}\text{V}_{6.25}$, $\text{Ti}_{50}\text{Pt}_{43.75}\text{Ta}_{6.25}$, and $\text{Ti}_{50}\text{Pt}_{43.75}\text{Hf}_{6.25}$ are the most

favourable structures, which is in agreement with DOS results. Addition of V, Ta and Hf stabilizes the B2 TiPt and TiPtM (M=V, Ta, Hf) ternary alloys are mechanically stable due to their C_{ij} 's satisfying the cubic stability conditions. TiPtM (M=V, Ta, Hf) ternary alloys become vibrationally stable as the content material of V, Ta and Hf increases in the system. The findings showed that the addition of V, Ta and Hf stabilizes the B2 TiPt alloys, however, they lower the martensitic transformation temperature of TiPt similarly to those reported for Co addition. However, the quaternary addition of Ta to TiPtCo are being suggested as a possible alloying element to enhance the transformation temperatures.

In chapter 6, the effect of Ta addition to B2 and B19 TiPtCo systems has been investigated. It is found that the $\text{Ti}_{50}\text{Pt}_{43.75-x}\text{Co}_{6.25}\text{Ta}_x$ is thermodynamically stable with 6.25 at.% Ta being favourable. The addition of 6.25 at.% Ta on $\text{Ti}_{50}\text{Pt}_{31.25-x}\text{Co}_{18.75}\text{Ta}_x$ was found to be the most favourable due to low ΔH_f . DOS suggest that 18.75 and 12.50 at.% Ta are the most stable alloys for $\text{Ti}_{50}\text{Pt}_{43.75-x}\text{Co}_{6.25}\text{Ta}_x$ and $\text{Ti}_{50}\text{Pt}_{31.25-x}\text{Co}_{18.75}\text{Ta}_x$, respectively. All the B2 quaternary alloys were mechanical stable. More importantly, the structure becomes vibrationally stable with an increase in Ta content material for both $\text{Ti}_{50}\text{Pt}_{43.75-x}\text{Co}_{6.25}\text{Ta}_x$ and $\text{Ti}_{50}\text{Pt}_{31.25-x}\text{Co}_{18.75}\text{Ta}_x$.

Both the B19 $\text{Ti}_{50}\text{Pt}_{43.75-x}\text{Co}_{6.25}\text{Ta}_x$ and $\text{Ti}_{50}\text{Pt}_{31.25-x}\text{Co}_{18.75}\text{Ta}_x$ alloys were found to be thermodynamically stable with 6.25 at.% Ta being the most favourable structures. The elastic constants showed that both $\text{Ti}_{50}\text{Pt}_{43.75-x}\text{Co}_{6.25}\text{Ta}_x$ and $\text{Ti}_{50}\text{Pt}_{31.25-x}\text{Co}_{18.75}\text{Ta}_x$ are mechanically stable and ductile ($B/G > 1.75$). The $\text{Ti}_{50}\text{Pt}_{43.75-x}\text{Co}_{6.25}\text{Ta}_x$ system is vibrationally stable which is in good agreement with the predicted elastic constants. Moreover, $\text{Ti}_{50}\text{Pt}_{31.25-x}\text{Co}_{18.75}\text{Ta}_x$ become vibrationally stable as the Ta content is increased, except for the 6.25 at.% Ta which showed the presence of soft modes.

The predicted transformation temperature for the most stable compositions, $\text{Ti}_{50}\text{Pt}_{37.50}\text{Co}_{6.25}\text{Ta}_{6.25}$ and $\text{Ti}_{50}\text{Pt}_{25}\text{Co}_{18.75}\text{Ta}_{6.25}$ are 500 K and 600 K, respectively. These temperature predictions can also suggest regions in which feasible martensitic transformations are probably, and was confirmed from the structural patterns using the X-ray diffraction (XRD). These findings suggest that the transformation temperature may decrease with the addition of Ta in the system. The temperature was reduced for the quaternary system, this may suggest that other alloying elements be investigated to check their potential.

Recommendations and future work

Several recommendations for future research are listed below:

- I. Energies of TiPtCo-M system as a function of occupation variables for each lattice position using Cluster Expansion.
- II. Investigate other alloying elements to check their potential.

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APPENDIX A

PUBLICATIONS AND CONFERENCE PRESENTATIONS

Presentations

1. Computational modelling of binary titanium based shape memory alloys (Oral), SAIP Conference, University of Free State, Bloemfontein, 2018.
2. The Ab initio study of $\text{Ti}_{50}\text{Pt}_{50-x}\text{M}_x$ ($\text{M}=\text{Ta}, \text{Hf}$; $x=6.25, 18.75, 25$) shape memory alloys (Oral), Faculty of Science and Agriculture Research day, Fusion Boutique, Polokwane, 2018.
3. Computational modelling of Potential binary Ti-based shape memory alloys (Oral), CoSAAMI, Riverside Sun, Vanderbijlpark, 2018.
4. The Ab initio study of $\text{Ti}_{50}\text{Pt}_{50-x}\text{Ta}_x$ ($x=6.25, 18.75, 25$) shape memory alloys (Poster), CHPC Conference, Century City Hotel, Cape Town, 2018.
5. The Ab Initio Study of $\text{Ti}_{50}\text{Pt}_{50-x}\text{Hf}_x$ ($x = 6.25, 18.75, 25$) Potential Shape Memory Alloys (Oral), SAIP Conference, Protea Hotel The Ranch Resort, Polokwane, 2019.
6. Structural, Elastic and Electronic Properties of $\text{Ti}_{50}\text{Pt}_{50-x}\text{Ta}_x$ as Potential High-Temperature Shape Memory Alloy (Oral), Faculty of Science and Agriculture Research day, Protea Hotel The Ranch Resort, Polokwane, 2019.
7. Effect of Tantalum on cubic B2 $\text{Ti}_{50}\text{Pt}_{50}$ Structure (Oral), CoSAAMI, Riverside Sun, Vanderbijlpark, 2019.

8. Effect of Ta, Hf and V on Structure and Stability of $\text{Ti}_{50}\text{Pt}_{50}$ shape memory alloys (Poster), CHPC Conference, Birchwood Hotel, Johannesburg, 2019.

Publications

1. Baloyi ME, Modiba R, Chauke HR and Ngoepe PE, **Computational study of binary titanium-based potential shape memory alloys**, Material Science and Engineering, **430**, (2018) 012020.
2. Modiba R, Baloyi E, Chikosha S, Chauke HR and Ngoepe PE, **Computational modelling of $\text{Ti}_{50}\text{Pt}_{50-x}\text{V}_x$ potential shape memory alloys**, Material Science and Engineering, **430**, (2018) 012021.
3. Baloyi ME, Modiba R, Chauke HR and Ngoepe PE, **Structural, elastic and electronic properties of binary titanium-based shape memory alloys**, *Proceedings of SAIP2018, the 63rd Annual Conference of the South African Institute of Physics*, (2019) 8-13.
4. Baloyi ME, Modiba R, Chauke HR and Ngoepe PE, **Ab initio study of $\text{Ti}_{50}\text{Pt}_{50-x}\text{Hf}_x$ ($x = 6.25, 18.75, 25$) potential shape memory alloys**, *Proceedings of SAIP2019, the 64th Annual Conference of the South African Institute of Physics*, (2020) 18-22.

Awards

2. MSc 4th Prize. The Ab initio study of $\text{Ti}_{50}\text{Pt}_{50-x}\text{M}_x$ ($\text{M}=\text{Ta}, \text{Hf}; x=6.25, 18.75, 25$) shape memory alloys (Oral), Faculty of Science and Agriculture Research day, Fusion Boutique, Polokwane, 2018.