A COMPARATIVE ASSESSMENT OF THE STRUCTURAL, ELASTIC AND ELECTRONIC PROPERTIES OF NB3PT AND NBPT3 PHASES THROUGH FIRST-PRINCIPLES STUDY

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ABSTRACT

Two phases of the Nb-Pt system namely Nb_3Pt and $NbPt_3$ have been studied using first principles approach in CASTEP. Structural, elastic and electronic properties of the concerned binary alloys were determined and examined against each other. Although both alloys have the same structure, it was observed that the percentage difference in the change of lattice parameters varied. Nb_3Pt exhibited a 0.073% change while $NbPt_3$ had a 14.809% change making Nb3Pt more stable struturaly than NbPt3. The elastic properties showed that both binaries are ductile materials but $NbPt_3$ proved to be more ductile than Nb_3Pt based on Born, Pugh's and Frantsevich's criteria. Through the electronic properties, both binaries were proven to be conducting and their bonding nature seen as a combination of ionic metallic and covalent bond.

1. INTRODUCTION

The platinum group metals (PGMs) which include osmium, iridium, ruthenium, rhodium, platinum and palladium have been of paramount usefulness in many technologies. In the petroleum, automotive and chemical industry, PGMs have been extensively used as core ingredients in the manufacture of catalysis. Their alloys are also found in electronic and aeronautic components (1). According to Ramesh et al. (2), the large enthalpy of formation of intermetallic compounds of Pt with early transition metals contribute to their stability as electrode catalyst compared to the conventional late transition metals alloys. The direct chemical energy conversion in PMFCs leading to its high efficiency is associated to the catalysis made of Pt. Unfortunately, carbon monoxide contained in the fuels is source of poisoning to the platinum based metal catalysts. Therefore, alloying Pt with metalloids and or late transition metals can help increase the catalytic performance as well as the poisoning tolerance.

According to Dew-Hughes (3), Hardy and Hulm discovered superconductivity in 1953 in compounds with the A-15 structure. The structure generally occurs near to the A3B stoichiometric ratio where A atoms are the transition metals Ti, Zr, V, Nb, Ta, Cr, and Mo while B atoms are more widely spread, but come mainly from periodic groups IIIB and IVB, and the precious metals Os, Ir, Pt, and Au. It is said that many of these have the same structure type but with different compositions of occupancies, for example, AB_3 and A_3B (4).

Six nonstoichiometric intermetallic compounds exist in the Nb-Pt (Niobium-Platinum) system according to Tripathi et al. (5). These include Nb_3Pt, Nb_2Pt, Nb_l-xPt_l +x, α'Pt, $NbPt_2$, and $NbPt_3$. Of considerable interest here are the Nb_3Pt and $NbPt_3$ phases first because they are formed at relatively the same temperature and second because they have the same structure type but with different compositions of occupancies. Although two polymorphs of $NbPt_3$ were identified and characterized by Tripathy et al. (5); that is the orthorhombic low-temperature form, α$NbPt_3$; and monoclinic high-temperature modification, βNbPt3, they concluded that Nb_3Pt is a highly ordered and more stable phase. Waterstrat and Giessen (6) found that α$NbPt_3$ and β$NbPt_3$ might be the same just that β$NbPt_3$ may have a higher Pt content than α$NbPt_3$. Meanwhile, a later work by Ramesh et al. (2) suggest that $NbPt_3$ intermetallic nanoparticles are highly stable and can be used as cotolerant electrocatalyst for fuel oxidation. Both Tripathy et al. (5) and Ramesh et al. (2) works were experimental and according to Huhn (7), just because a particular phase is experimentally observed does not mean that it is stable. To determine the stability of a phase, it is necessary to find its free energy and show that out of all possible phases, it is this phase that has the lowest free energy, a process known as "free energy minimization."

Huhn, (7) asserts that because of their high degree of accuracy without the usage of any fitting parameters, first principles calculations have become one of the main computational methods in condensed matter physics and physical chemistry. The Cambridge Serial Total Energy Package (CASTEP) programme is known as a first principles quantum mechanical code for performing electronic structure calculations. Clark et al. (8) explained that the molecular dynamics implementation in CASTEP follows the Born-Oppenheimer approximation where the forces are calculated from the ground state electronic configuration at each molecular dynamic step. The constant-energy, constant-volume ensemble (NVE); the constant-temperature, constant-volume ensemble

(NVT); the constant-pressure, constant-enthalpy ensemble (NPH) and the constant-temperature, constant-pressure ensemble (NPT) ensembles can be simulated within the scheme. Depending on which state variables (the energy *E*, volume *V*, temperature *T*, pressure *P*, and number of particles *N*) are kept fixed, different statistical ensembles can be generated. The regulation of the hydrostatic pressure is done through the use of either an Andersen-Hoover or Parrinello-Rahman barostat. Temperature control is implemented via a chain of Nose-Hoover thermostats or by performing Langevin dynamics in the appropriate phase space.

A number of researchers have successfully used CASTEP program as tool for the first principle study of several intermetallics (9 – 19). Related to the current work are the investigations of Li et al. (9) and Naher et al. (11)) because they both investigated the structural, elastic and electronic properties of Nb_3Pt with respect to Nb_3Ir and Nb_3Os respectively. They both found that the computational results were well in agreement with the experimental results found in the literature. Li et al concluded that Nb_3Ir should have better structural stability than Nb_3Pt while Nahera et al concluded that Nb_3Os is expected to have good lubricating properties compared to Nb_3Pt. Both conclusions again bring into fore the question of how stable the Nb3Pt phase of the NbPt intermetallic is. So far, no literature has been found on the first principle study of $NbPt_3$ phase using the CASTEP programme and no direct comparison of the electronic, structural and elastic properties of both phases has been made.

This study aims at eliminating the controversy that exist in acknowledging which phase of Nb-Pt is more stable than the other using first principle calculation which has been validated as a suitable way of proving the ground state of structures. Generated data for direct comparison will be made available and will be useful to designers and researchers.

2. MATERIALS AND METHODS

The fcc structure atoms are located at each of the corners and the centers of all cubic faces. Each of the corner atoms is the corner of another cube so the corner atoms are shared among eight unit cells.

Pt is a face centered cubic structure with a space group symmetry Fm-3m and pearson symbol cF4. The experimental lattice parameter of Pt at room temperature is 3.924 °A (20).

The bcc unit cell has atoms at each of the eight corners of a cube plus one atom in the center of the cube. Each of the corner atoms is the corner of another cube so the corner atoms are shared among eight unit cells. It is said to have a coordination number of 8.

Nb has a body-centered structure with a space group Pm-3m and pearson symbol cP2, the experimental lattice parameter of Nb is 2.884. Figure 1 shows the orthographic display of atoms before geometry optimization while Figure 2 shows that of the binaries Nb_3Pt and $NbPt_3$

All calculations were carried out using the CASTEP code a (8).

The configurations of valence electron used were $4s^2\ 4p^6\ 4d^4\ 5s^1$ for Nb and $5d^9\ 6s^1$ for Pt. Mulliken atomic population was used as well

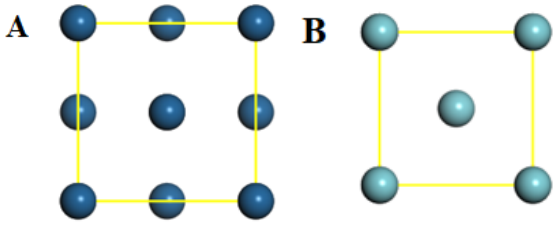

Figure 1: Orthographic display of atoms before geometry optimization A) Pt and B) Nb

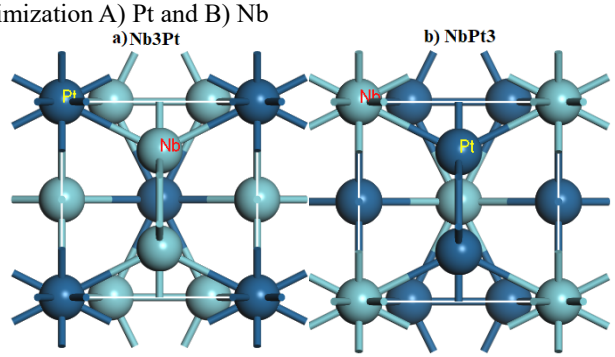

Figure 2: Orthographic display of the binaries A) Nb_3Pt and B) $NbPt_3$

For the energy calculation, Koelling-Harmon was used for the relativistic treatment and the pseudopotentials under ultrasoft with a medium tolerance. Energy was calculated under Local Density Approximation (LDA). Geometry optimization was conducted under the same conditions with the exception that further optimization under Generalized Gradient Approximation (GGA) was done to compare energy minimization during geometry optimization.

The electronic properties of the structures were evaluated under GGA where the band structure and the density of state of both binaries were determined and compared. The mechanical properties represented by the evaluation of the elastic constant was examined under GGA as well and determination of bulk modulus, young's modulus were achieved. The well-established Voight–Reuss–Hill (VRH) approximations validated in many metallic and insulating materials are used to calculate the polycrystalline bulk elastic properties, namely, bulk modulus B and shear modulus G from calculated Ci j. (21).

3. RESULTS AND DISCUSSION

3.1 Structural Properties

The optimized structure of individual molecules resulted in a more packed and organized structure as can be seen in figure 3. Achieving the desired optimized structure through attaining

the appropriate cut-off energy and suitable k-point followed the trend in figure 4 and 5. The determined parameters are shown in Table 1. The determined cut-off energy and total energy are approximately the same for Pt and Nb molecules when calculated in LDA or GGA. There is a considerable change in lattice parameter as observed from the obtained values. For Platinum, we have 3.9239 Å before optimization and 2.7722 Å after. The same goes for Niobium, 3.3006 Å before and 2.8118 Å . That is approximately 70.6 and 85.2 % structural adjustment in respective molecules after optimization.

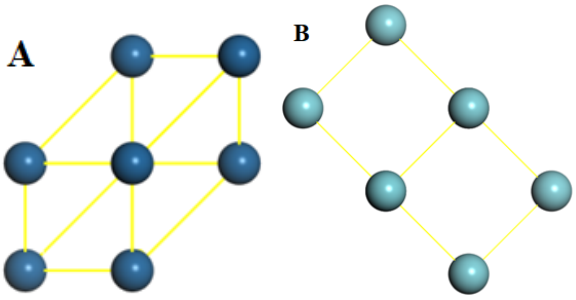

Figure 3. Orthographic display of atoms after geometry optimization A) Pt and B) Nb

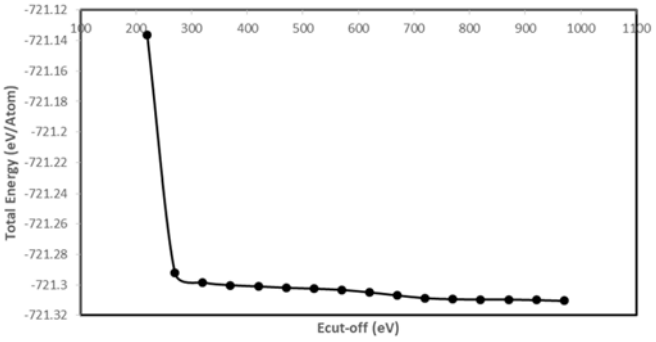

Figure 4: Total energy vs kinetic energy cut-off for Pt

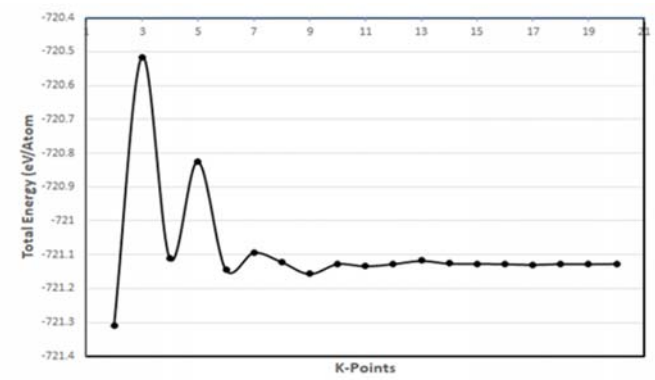

Figure 5: Total energy vs k-points for Pt

Table 1: Energy cut-off, total energy and laticce parameters for pure Pt and Nb as calculated

Materials	**Ecut-off(eV)**	**ETotal(kJ/mol)**		**a (Å)**
		LDA	GGA	
Pt	870	-721.1276	-718.1708	Before: 3.9239 After: 2.7722
Nb	780	-1549.3042	-1551.3042	Before: 3.3006 After: 2.8118

Structural optimization of the binaries were conducted using cut –off energy values of 1530 eV at 16x16x16 k-point for Nb_3Pt and 1480 eV for $NbPt_3$ at 17x17x17 k-point given the cubic structures. The derived lattice parameters exhibited little difference from the original ones with 0.073% for Nb_3Pt and 14% for $NbPt_3$ as seen in Table 2.

Table 2: Energy cut-off, total energy and lattice parameters for pure Nb_3Pt and $NbPt_3$ binaries as calculated

Materials	**Ecut-off (eV)**	**K-points**	**ET (kJ/mol)**		**a (Å)**	
			LDA	GGA		% Difference
Nb3Pt	1530	16x16x16	-10741.6899	-10749.7494	Before: 5.110 After: 5.106	0.073150
NbPt3	1480	17x17x17	-7429.7068	-7416.4859	Before: 5.110 After: 5.018	14.8094

3.2 Elastic Properties

The importance of determining the elastic constant for intermetallic materials cannot be overemphasized because they are tightly related to the nature of electronic bonding among the atoms. Furthermore, the elastic constants give relationships connecting the dynamical and mechanical properties of crystalline materials.

Based on Born Criteria (22) for mechanical stability which says that for a system to be mechanically stable the following conditions should be met: $C_{11} > 0$, $(C_{11} \_ C_{12}) > 0$, $C_{44} > 0$ and $(C_{11} + C_{12})C_{33} > 2C_{13}^2$. One binary is stable ($Nb_3Pt$) while the other ($NbPt_3$) is not because as seen in Table 3, C44<0 (- 60.670) for NbPt3. Pugh's criterion (23) is mainly based on shear modulus and bulk modulus and says that for G/B>0.5 the material is brittle and if G/B<0.5 the material is ductile. The shear modulus describes the material's response to shearing strains i.e., the resistance to change in shape and the bulk modulus describes the material's response to uniform pressure. Both Nb_3Pt and $NbPt_3$ have B/G<0.5 as indicated in Table 3 making both ductile materials. But with B/G=0.160 for $NbPt_3$ much lower than B/G=0.391 for Nb_3Pt, $NbPt_3$ can be said to be more ductile than Nb_3Pt. This is also confirmed when considering the Frantsevic's rule (24) which says that Poisson Ratio $\nu \approx 0.33$ and that $\nu < 0.33$ indicates a brittle material while $\nu > 0.33$ indicates a ductile materials seen in Table 3. Poisson's ratio is often used in engineering science and it relates directly to the failure mode of solids. Nb_3Pt and $NbPt_3$ have $\nu > 0.33$ that is 0.326 for Nb_3Pt and 0.423 respectively suggesting that both binaries are ductile with $NbPt_3$ more ductile than its counterpart, The ratio of the bulk modulus B to C44 can be interpreted as a measure of plasticity (25). A large value of B/C_{44} indicates that the corresponding material has excellent lubricating properties. Based on the data obtained as indicated in Table 3, Nb_3Pt has better lubricating properties than $NbPt_3$ since its B/C_{44} ratio is larger.

Young's modulus, Y is defined as the ratio of longitudinal stress and longitudinal strain, is a measure of the stiffness of the solid material. The higher value of Y indicates higher stiffness of the material. The plasticity may also be estimated by the values of $(C_{11} - C_{12})$ and Young's modulus Y (26). The smaller values of $(C_{11} - C_{12})$ and Y indicate a better plasticity of Nb3Pt or $NbPt_3$. Here, Nb_3Pt has the smaller value for $(C_{11}\text{-}C_{12})$ = 306.137 but larger value of Young modulus. Meanwhile, $NbPt_3$ has the larger value of $(C_{11}\text{-}C_{12})$ which is 424.397 but smaller value of Young's modulus (138.062) making it difficult to apply this method to compare the plasticity of the binaries. Another way of determining the plasticity being the ratio B/C_{44} as indicated in Table suggests that Nb_3Pt has better lubricating properties than $NbPt_3$ since it has a larger B/C_{44} value

Table 3. Calculated single crystal elastic constants Ci j (GPa), polycrystalline bulk modulus B (GPa), shear modulus G (GPa), Young modulus Y (GPa), Pugh's ratio G/B, Poisson's ratio ν, and the measure of plasticity for Nb_3Pt and $NbPt_3$.

Single Crystal Elastic Properties			Polycrystalline Elastic Properties		
Properties	Nb_3Pt	$NbPt_3$	Properties	Nb_3Pt	$NbPt_3$
C_{11}	464.100	585.666	B	260.009	302.735
C_{12}	157.963	161.269	G	101.914	48.477
C_{13}	157.963	161.269	Y	270.411	138.062
C_{33}	464.100	585.666	G/B	0.391	0.160
C_{44}	67.811	- 60.670	ν	0.326	0.423
C_{66}	67.811	- 60.670	B/C_{44}	- 3.834	4.989

1.2 Electronic Properties

The optimized lattice parameter of Nb3Pt and NbPt3 were used to derive their respective band structures as shown in Figure 6 With Nb3Pt, the Fermi level which is set at 0 eV is crossed at 3 different bands from -1.028 to 0.677, -0.120 to 0.677 and from -0.027 to 0.870. The Fermi level in NbPt3 is crossed at 3 different bands as well from -0.779 to 0.954, -0.546 to 1.074 and from -0.516 to 1.457. These crossings show that both binaries are conducting. The total energy densities of state as seen in Figure 7 have values of 10 and 12 eV respectively at Fermi level for the binaries. There are several picks observed along the curves the highest ones being derived from the hybridization of Nb and Pt. The bonding nature of the binaries being seen as a combination of ionic metallic and covalent bond.

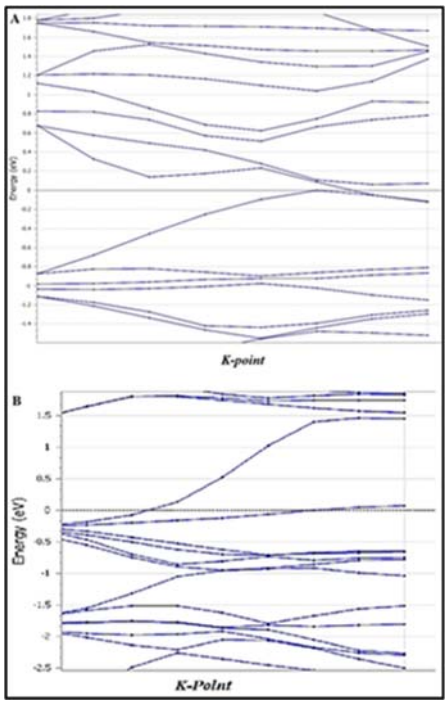

Figure 6. Band Structures plot. A. Nb_3Pt and B. $NbPt_3$

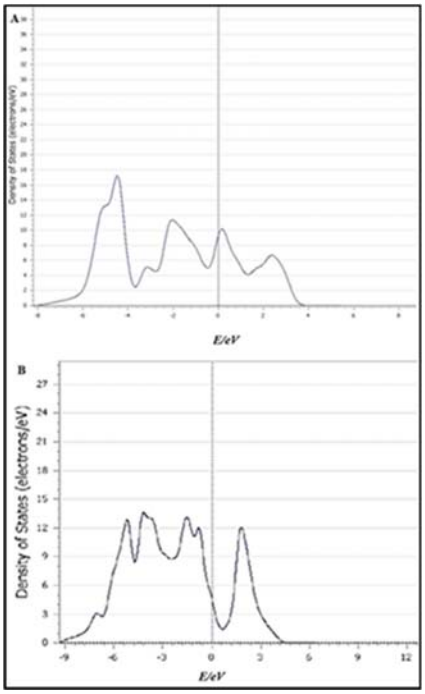

Figure 7. Total Density of State. A. Nb_3Pt and B. $NbPt_3$

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CONCLUSION

This work examined the structural, elastic and electronic properties of Nb_3Pt and $NbPt_3$ intermetallic binaries who are two phase of the Nb-Pt system. Based on obtained data from structural analysis, Nb_3Pt is more stable than $NbPt_3$ with a much lower percentage deviation of the lattice parameters. The elastic parameters show that both intermetallics are ductile in nature but $NbPt_3$ exhibit more ductility based on the data acquired. The electronic property show that there is a combination of ionic and covalent bond in the considered binaries. Knowing that $NbPt_3$ is made of two polymorphs; that is the orthorhombic low-temperature form, $\alpha NbPt_3$; and monoclinic high-temperature modification, βNbPt3, further analysis on their structural, elastic and electronic properties can provide better understanding on the nature of $NbPt_3$ as a superconducting intermetallic.

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