INVESTIGATION OF ELECTRONIC AND GROUND STATE PROPERTIES OF SOME METAL CARBIDES

SYNOPSIS

1.1 INTRODUCTION

Carbides are the compounds possess higher electronegativity, which are formed by carbon and metals. Based on the difference in electronegativity of metals and carbon, several classes of carbides are usually formed. The incorporation of carbon into the lattices of metals has demonstrated compounds with unique physical, chemical, electronic and catalytic properties. These resulting alloys are referred to as metal carbides. The carbides are well-known for their hardness, strength and high melting points. Interestingly, they also possess electronic and magnetic properties similar to those of metals. They often adopt simple crystal structures, such as face-centered cubic (fcc), body-centered cubic (bcc) or simple hexagonal structure, with the non-metal elements occupying the interstitial spaces between metal atoms.

The metal carbides formed are classified into three basic types according to general trends in their properties: ionic carbides, interstitial carbides and covalent carbides. Metal carbides constitute a diverse class of materials with many technological applications. Because of their great strength and durability, they have been traditionally used at extreme conditions of temperature and pressure, for example in rocket nozzles and drill bits. Their hardness has given them applications in cutting tools, the materials for machine-building, nuclear and chemical industries, in the production of structural ceramics, in manufacturing of abrasives,

protective coatings, wear-resistant materials, etc. However, they also have interesting optical, electronic and magnetic properties and they have been used for optical coatings, electrical contacts, diffusion barriers and other uses. These materials compromise structural components in automotive engines, gas turbine engines and other machinery as well as entering into several other aerospace and military applications. They form an essential part of ceramic industry throughout the world.

1.2 SCOPE OF THE STUDY

The scope of the present work is to study the ground state properties, electronic structure, mechanical and magnetic properties of metal carbides under normal and high pressures. More specifically, the aim of the present work is to determine the stability of metal carbides among the various considered structures.

1.3 OBJECTIVES OF THE STUDY

The objectives of the present study are:

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- To obtain the ground state properties like lattice parameter, cell volume, cohesive energy, formation energy, bond length, bulk modulus and its pressure derivative of some selected metal carbides.
- To investigate the structural stability and phase transition in metal carbides under normal and high pressure by computing the total energy.

- ❖ To investigate their electronic structure such as, band structure, total and partial density of states and charge density distribution at normal and high pressure.
- ❖ To estimate the elastic constants, bulk modulus, Young's modulus, shear modulus, Poisson's ratio, Pugh ratio (B/G) and hardness of some metal carbides.
- ❖ To analyze the magnetic properties of some metal carbides.

1.4 MATERIALS INVOLVED

The elements used in the framework of the present thesis are the elements which belong to the alkali elements, 4*d* and 5*d*-block elements. These elements are Lithium (Li), Sodium (Na), Potassium (K), Rubidium (Rb), Magnesium (Mg), Calcium (Ca), Ruthenium (Ru), Rhodium (Rh), Palladium (Pd), Osmium (Os), Iridium (Ir), Platinum (Pt), Silicon (Si) and Germanium (Ge). All these elements react with carbon and form metal carbides.

1.5 METHODOLOGY

The present work is theoretical and computational type based on modern density functional theory. The first principles calculations are performed based on density functional theory as implemented in VASP code.

1.6 ORGANIZATION OF THE THESIS

In the present work, the structural stability, electronic structure, mechanical properties, magnetic and optical properties of metal carbides are computed. The investigations carried out in the present work are distributed in seven chapters. The last chapter consists of the summary and conclusion.

- In the chapter I, the classification of metal carbides and its applications are discussed. The scope and objectives of the study, materials involved, review of literatures of the metal carbides are also discussed in first chapter. The theory of structural analysis, band structure, density of states, charge density distribution, elastic properties of material and spin alignment and magnetism are outlined.
- The *ab initio* calculations are performed using density functional theory as implemented in the Vienna ab initio simulation package (VASP). The Local Density Approximation (LDA) as well as Generalized Gradient Approximation (GGA) are used in VASP for exchange and correlation. The quantum mechanical description of many body systems, the density functional theory, the local density approximation (LDA), generalized gradient approximation (GGA), theory of VASP are discussed in Chapter II.
- In chapter III, the structural stability, structural phase transition, density of states, charge density distribution and elastic properties of transition metal carbides (RuC, RhC, PdC, OsC, IrC, PtC) are discussed. All these carbides are stable in zinc blende phase at normal pressure. A pressure-induced structural phase transition from ZB to NiAs phase is predicted in OsC, IrC and PtC. From density of states, it is seen that RuC exhibits semiconductor behavior in its stable phase while other carbides are found to be metallic in their stable structure. The bonding nature of these materials is found to be covalent-like due to the hybridization of C and metal atoms. The computed

elastic constants indicate that these carbides are mechanically stable at ambient pressure.

- In Chapter IV, the structural stability, electronic structure and elastic properties of noble metal carbides M_2C and MC_2 (TM = Os, Ir, Pt) are investigated in fluorite/anti-fluorite, pyrite, hexagonal, tetragonal and orthorhombic phases. Among the five crystallographic phases that have been investigated, the metal carbides M_2C are found to be stable in anti-fluorite structure, whereas MC_2 is stable in hexagonal structure. In Os_2C and Pt_2C, structural phase transition is predicted from antifluorite (AF) to pyrite, AF to hexagonal in Ir_2C and hexagonal to tetragonal in OsC_2 and PtC_2 is predicted under high pressure. The electronic structure reveals that these carbides are metallic. The calculated elastic constants indicate that these materials are mechanically stable at ambient condition. The Debye temperature values are reported for all the phases of these carbides. The high bulk modulus of these materials indicates that these materials are super hard materials.

- Chapter V presents the structural, electronic and mechanical properties of TM_2C and TMC_2 (TM = Ru, R, Pd) in tetragonal, antifluorite/fluorite, orthorhombic, pyrite, and hexagonal phase. Among the five crystallographic phases investigated, AF phase is the lowest energy phase for TM_2C (TM = Ru, R, Pd) whereas hexagonal phase is the lowest energy phase for TMC_2 (TM = Ru, R, Pd). A pressure induced structural phase transition is observed in all these carbides. The transition from AF to tetragonal phase, similarly in

Rh_2C, pressure induced phase transition from AF to orthorhombic phase and in Pd_2C a transition from AF to hexagonal is predicted. The transition from hexagonal to pyrite structure is predicted for RuC_2 and on further increasing the pressure, pyrite to orthorhombic transition is predicted. Hexagonal to orthorhombic phase transition is observed in RhC_2 and PdC_2. The electronic structure of noble metal carbides TM_2C and TMC_2 (TM = Ru, Rh, Pd) confirm their metallic nature. The computed elastic constants obey the necessary mechanical stability conditions suggesting that all the carbides are mechanically stable in all the considered phases. Moreover, these metal carbides are classified as hard materials.

- Chapter VI contains results of the investigation of the electronic structure of silicon carbide with increasing germanium content for two different phases, namely, cubic zinc blende and hexagonal phases. The zinc blende structure is found to be the stable one for all the $Si_{1-x}Ge_xC$ semiconducting carbides at normal pressure. Effect of substitution of Ge for Si in SiC on electronic properties is studied. It is observed that cubic SiC is a semiconductor with the band gap value 1.243 eV. The band gap value of SiC is increased due to the substitution of Ge and the band gap values of $Si_{0.75}Ge_{0.25}C$, $Si_{0.50}Ge_{0.50}C$, $Si_{0.25}Ge_{0.75}C$ and GeC are 1.322 eV, 1.413 eV, 1.574 eV and 1.657 eV respectively. As the pressure is increased, it is found that the energy gap get decreased for $Si_{1-x}Ge_xC$ (X = 0, 0.25, 0.50, 0.75, 1). The elastic constants satisfy the Born – Huang elastic stability criteria. The bulk modulus, shear modulus, Young's modulus and Poisson's ratio are also

calculated and compared with the other available results. The optical parameters of these cubic carbides correspond to UV region. Hence, these materials can be used in UV photo detectors and photovoltaic applications.

- Chapter VII deals with the electronic structure, magnetic and mechanical properties of AMXC (AM = Li, Na, K, Rb, X = Mg, Ca) in half – Heusler ($C1_b$) type structure are computed for various phases such as α, β and γ phases. The β phase is found to be the most stable one for these carbides at normal pressure. A structural phase transition from β to α phase in NaMgC and β to γ phase in RbMgC is predicted. From the total energy spin polarized calculations, these compounds are found to be more stable in ferromagnetic phase than non – magnetic phase except LiMgC. Ferromagnetic to non – magnetic phase transition is predicted in KMgC, NaCaC and RbCaC. Spin polarized density of states of AMXC (AM = Na, K, Rb, X = Mg, Ca) compounds confirms the existence of half metallic ferromagnetism with 100% spin polarization around the Fermi level. The density of states of LiMgC shows the absence of spin polarization and it confirms the non-magnetic nature. The calculated elastic constants satisfy the stability criteria and hence these carbides are mechanically stable in their most stable phase. The bulk modulus, shear modulus, Young's modulus and Poisson's ratio are also calculated.
- The results of the research work and the conclusions are summarized in the last chapter VIII as "Summary and Conclusions".