Electronic structure, bonding behavior and optical properties of $(HfC)_mAl_4C_3$ (m = 1, 2, 3) carbides

Salman Mehmood [a], *, Athar Javed [b], Muhammad Nasir Rasul [a], Muhammad Azhar Khan [a], Altaf Hussain [a], **

[a] Department of Physics, The Islamia University of Bahawalpur, Bahawalpur, 63100, Pakistan
[b] Department of Physics, University of the Punjab, Lahore, 54590, Pakistan

ARTICLE INFO

ABSTRACT

This paper reports results from the study of the electronic structure, bonding and optical properties of ternary $(HfC)_mAl_4C_3$ (m = 1, 2, 3) carbides. The interatomic bonding and bond order is studied to elucidate the role to atoms in the structure. The band structures of all three ($HfAl_4C_4$, $Hf_2Al_4C_5$ and $Hf_3Al_4C_6$) carbides show conducting nature. All three carbides exhibit direct band gap. Density of states (DOS) spectra of $HfAl_4C_4$, $Hf_2Al_4C_5$ and $Hf_3Al_4C_6$ carbides reveal that the total number of states, $N(E_F)$ at Fermi level are 2.84, 6.51 and 6.37 states/eV, respectively. The electronic charge transfer from Hf and Al atomic sites to C atomic site has been found in all three carbides. The bond order (BO) calculation of these carbides shows the dominating role of Al-C bonds in to the cohesion of crystal structures. Localization index (LI) calculation reflects highly delocalized states near the Fermi level. The dependence of dielectric function and optical conductivity on photon energy show anisotropic behavior of $HfAl_4C_4$, $Hf_2Al_4C_5$ and $Hf_3Al_4C_6$ carbides.

1. Introduction

Hafnium carbide (HfC) is the most refractory binary ceramic carbide which belongs to the transition metal carbides (TMCs) group [1,2]. Being a ceramic material with high melting point (~3900 °C), HfC has excellent mechanical and chemical properties. A good wear resistance and chemical inertness of HfC makes it a promising ceramic material for various applications [3–7]. For example, HfC has applications in ultra-high temperature environment such as in rockets, scramjet engines, re-entry vehicles and thermal protecting system for hypersonic vehicles. The HfC has also potential application as a fuel and structural matrix material in nuclear reactors [8–12]. However, poor degree of oxidation resistance and brittleness limits its applications and reliability [13,14]. To overcome these weaknesses, several efforts have been made by various research groups, see for example Refs. [15,16]. Similar to TAX or MAX phase materials [16], the ternary carbides generally

represented by formula $T_{n+1}AX_n$ (where T = element from early transition metals, A = A group element such as aluminum, X = C or N and n = 1, 2, 3 …) offers to improve the ductility and degree of oxidation resistance by adding Al in binary carbides [17–19]. Ternary aluminum carbides such as ZrAlC and HfAlC with different compositions have been successfully synthesized in laboratory and experimental results on structural and mechanical properties have been reported in Refs. [20–26]. Studies show that the degree of oxidation resistance, mechanical strength, specific stiffness and/or fracture toughness of ternary (HfAlC and ZrAlC) carbides has significantly improved as compared to binary (ZrC and HfC) carbides [25–31].

Ternary Hf-Al-C system has several crystallographic phases. For example, ternary $Hf_2Al_3C_4$ and $Hf_3Al_3C_5$ carbides exhibit hexagonal symmetry with space group $P6_3/mmc$. Both $Hf_2Al_3C_4$ and $Hf_3Al_3C_5$ systems are iso-structural to $Zr_2Al_3C_4$ and $Zr_3Al_3C_5$ [32–35]. He et al. [25] found new phases ($Hf_2Al_4C_5$ and $Hf_3Al_4C_6$) of Hf–Al–C ceramics. $Hf_2Al_4C_5$ and $Hf_3Al_4C_6$ are similar to $Zr_2Al_4C_5$ [36] and $Zr_3Al_4C_6$ [37], respectively but dissimilar to $Hf_2Al_3C_4$ and $Hf_3Al_3C_5$ ceramics. Both $Hf_2Al_4C_5$ and $Hf_3Al_4C_6$ carbides exhibit space group $R\bar{3}m$; while $Hf_2Al_3C_4$ and $Hf_3Al_3C_5$ carbides has space group $P6_3/mmc$. The $Hf_2Al_3C_4$ and $Hf_3Al_3C_5$ belong to homologous series of HfAlC phases [20,21,38] with general formula $(HfC)_mAl_3C_2$ (m = 2

---

* Corresponding author.
** Corresponding author.
   E-mail addresses: salman.mehmood@iub.edu.pk (S. Mehmood), haltafphy@iub.edu.pk (A. Hussain).

Table 1
Crystal and electronic structure data of $HfAl_4C_4$, $Hf_2Al_4C_5$ and $Hf_3Al_4C_6$.

$(HfC)_mAl_4C_3$	$m = 1$	$m = 2$	$m = 3$
	$HfAl_4C_4$	$Hf_2Al_4C_5$	$Hf_3Al_4C_6$
Crystal Structure data			
Crystal system	Hexagonal	Hexagonal	Hexagonal
Space group	$P\bar{3}m1$ (No. 164)	$R\bar{3}m$ (No. 166)	$R\bar{3}m$ (No. 166)
Lattice parameters			
a (Å)	3.308	3.274	3.265
b (Å)	3.308	3.274	3.265
c (Å)	21.900	40.220	48.090
α	90.00	90.00°	90.00°
β	90.00	90.00°	90.00°
γ	120.00	120.00°	120.00°
Volume (Å^3)	207.536	373.362	443.968
Formula units/unit cell	2	3	3
Atoms/unit cell	18	33	39
SCF k-points	513 ($18 \times 18 \times 3$)	148 ($12 \times 12 \times 2$)	148 ($12 \times 12 \times 2$)
OLCAO k-points	1201 ($24 \times 24 \times 4$)	1160 ($24 \times 24 \times 4$)	1160 ($24 \times 24 \times 4$)
Non-equivalent sites	10	6	7
Atom types (no. of atoms of different type)			
Hf	1 (2)	1 (6)	2 (3, 6)
Al	4 (2, 2, 2, 2)	2 (6, 6)	2 (6, 6)
C	5 (1, 2, 2, 2, 1)	3 (3, 6, 6)	3 (6, 6, 6)
Electronic structure information			
Upper VB width (eV)	8.13	6.98	6.92
Lower VB width (eV)	4.94	4.59	4.55
Energy gap between lower and upper VB (eV)	1.06	1.98	1.91
DOS at Fermi level $N(E_F)$	2.84	6.51	6.37

and 3); whereas $Hf_2Al_4C_5$ and $Hf_3Al_4C_6$, have chemical formula $(HfC)_mAl_4C_3$ (m = 2 and 3).

Nian et al. [39] synthesized new $HfAl_4C_4$ ternary carbide and studied its microstructural properties using XRD and TEM. They also studied the mechanical properties of $HfAl_4C_4$ by first principles approach [39]. He et al. [25] also reported the elastic and mechanical properties of $Hf_2Al_4C_5$, $Hf_3Al_4C_6$, $Hf_2Al_3C_4$ and $Hf_3Al_3C_5$ carbides along with HfC (cubic), HfC (hexagonal) and Al_4C_3. They found that the mechanical properties (elastic stiffness constants, bulk modulus, shear modulus and elastic modulus) depended on the Al-C and Hf-C slab thickness in Hf-Al-C structure. Further, they concluded that the $Hf_3Al_4C_6$ was stiffer and stronger as compared to $Hf_2Al_4C_5$ [25]. Until now, though some theoretical calculations have been carried-out to study the elastic and mechanical behavior of Hf-Al-C carbides [25,39], the electronic structure, bonding behavior and optical properties of $HfAl_4C_4$, $Hf_2Al_4C_5$ and $Hf_3Al_4C_6$ have not been studied so far.

In this paper, theoretical results on the electronic structure, bonding and optical properties of three ternary $HfAl_4C_4$, $Hf_2Al_4C_5$ and $Hf_3Al_4C_6$ carbides are reported. First principles calculations have been performed by implementing the orthogonalized linear combination of atomic orbitals (OLCAO) method [40]. The band structures, bonding and optical properties of $HfAl_4C_4$, $Hf_2Al_4C_5$ and $Hf_3Al_4C_6$ carbides are discussed and correlated with structural properties. The localization index (LI) and effective charge (Q^*) behavior is also discussed for better understanding of electronic and optical behavior of $HfAl_4C_4$, $Hf_2Al_4C_5$ and $Hf_3Al_4C_6$ carbides.

2. Computational detail

For theoretical calculations of ternary $(HfC)_mAl_4C_3$ (m = 1, 2, 3) carbides, first principles calculations were performed by implementing OLCAO method based on density functional theory [40,41]. In order to study the structure, bonding and optical behavior of three ternary $HfAl_4C_4$, $Hf_2Al_4C_5$ and $Hf_3Al_4C_6$ carbides, results were produced by applying OLCAO method. OLCAO is a well-established code which offers to calculate electronic structure, chemical

bonding and optical properties of crystalline [42,43] materials [42−45]. The exchange-correlation energy functional is calculated by applying local density approximation (LDA) [46]. For $(HfC)_mAl_4C_3$ (m = 1, 2, 3) carbides, the initial structural model with lowest energy has been utilized as described by Nian et al. [39]. In OLCAO method, the wave functions of atomic orbitals are expanded considering Gaussian type orbitals (GTOs). The quantization of angular momentum is applicable to spherical harmonics. To extract different properties, three basis sets are implemented in OLCAO method. Firstly, the full basis (FB) set is used in the calculation of self-consistent field (SCF) potential, band structures and density of states (DOS). For each atom, the FB set consists of core electron orbitals, occupied valence electron orbitals and empty shell of unoccupied electron orbitals. For Hf-Al-C system, the FB set consists of Hf-(1s, 2s, 2p, 3s, 3p, 3d, 4s, 4p, 4d, 5s, 5p, 4f, 5d, 6s, 6p, 6d, 7s, 7p, 7d, 8s and 8p), Al-(1s, 2s, 2p, 3s, 3p, 3d, 4s, 4p, 4d, 5s and 5p) and C-(1s, 2s, 2p, 3s, 3p, 4s and 4p). Secondly, an extended basis (EB) set is applied in calculating optical properties. In this case, one additional shell of empty orbitals is included in order to improve the accuracy of higher energy states in the conduction band. Third one is a minimal basis (MB) set which is used for effective charge (Q^*) and bond order (BO) calculations using Mulliken analysis [47]. MB set provides more localized basis in calculating Q^* and BO. To obtain self-consistency in calculating the crystal potential, the total energy is allowed to converge to minimum value 0.0001a.u. To run simulations, a sufficient number of k-points are necessary for SCF iterations and to obtain optical spectra (see Table 1). The BO and Q^* are calculated by using the method described elsewhere [43].

3. Results and discussion

3.1. Crystal structure and atomic bonding

Ternary $(HfC)_mAl_4C_3$ (m = 1, 2, 3) carbides have hexagonal ($a = b \neq c$) crystal structures. The $HfAl_4C_4$ has space group $P\bar{3}m1$ (SG. No. 164) while both $Hf_2Al_4C_5$ and $Hf_3Al_4C_6$ carbides have space group $R\bar{3}m$ (SG. No. 166) [25,39]. There are two formula units with 18