Spectroscopic Properties of Ta Doped NbS By Using First Principles Calculations

Sobia Manzoor and Sikander Azam

February 26, 2020

Spectroscopic Properties of Ta Doped NbS By Using First Principles Calculations

Sobia Manzoor[1], **Sikander Azam**[2],

[1]*Department of Physics The University of Lahore, Sargodha Campus, Sargodha, Pakistan*

[2]*Department of Physics Riphah International University Sector I-14 Islamabad, Pakistan.*

Abstract

For the $Ta_xNb_{1-x}S$ electronic, optic and structural properties are calculated by using extremely accurate all electrons FP–LAPW [full potential linearized augmented plane wave] method. The lattice constants calculated theoretically are established to be in fine agreement with the values that are measured experimentally. It is established that every one of these compounds are indirect and wide band gap semiconductors and this band gap is to be found at X and M-symmetry point, whereas the band gap decreases from S to Se. Optical properties like imaginary and real components of dielectric functions, extinction coefficients, refractive indices, reflectivities, absorption coefficients, and optical conductivities are also calculated for these compounds. High absorption power and the direct band gap characteristics of these compounds in the UV-Visible energy range indicates that these perovskite structures might be used in optoelectronic and optical devices working in the UV-Visible range of the energy spectrum.

1.1 Introduction

2H-NbS**2** relates to the group of layered transition metal (IVB, VB and VIB) dichalcogenides. As in an primitive review paper by Wilson and Yoffe (1969), layered transition metal dichalcogenides have a structure compose from "molecular sandwiches", each sandwich consist of a sheet of transition metal atoms in between two sheets of chalcogen atoms. The atoms in a sandwich are not tightly packed through strong and chiefly covalent bonds, while the sandwiches are held together by weak van der Waals forces.

The sandwich consists of three layers of hexagonally packed atoms is known as molecular layer. Due to this argument the names of "layer material" and "layer compounds" are also relate and use for layered transition metal dichalcogenides. Depending on the stacking sequence and order of the layers, there are number of poly types in layered materials, particular in the group VR materials. Majority of the elements of the other groups stand up into just one co-ordination class. So far as we know, NbS2 consists of only 2H and 3R poly types (Fisher and Sienko, 1380). In this abbreviated notation, the integer represents the number of layers per unit cell along the hexagonal symmetry axis (c,z), and T, H,Rh denoted the trigonals, hexagonal and rhombohedral primitive unit cells respectively, In the 1T poly type of TaS2, for example, the Ta atom is octahedral coordinated by sulphur atoms while in the 2H phase the co-ordination is trigonal prismatic.the 4Hb and 6R poly types, the co-ordination within successive layers alternates between octahedral and trigonal prismatic

Group V consists of large number of free carriers due to the fact that is so-called dZ2 band is only half full. These free carriers are liable for move up (rise) in absorptions underneath around the value of 1 eV. Compounds of group VI demonstrate the dZ2 band is full and shows the semi-conducting behavior comes out (results). Group IV, V and VT layer compounds reflect a solid (strong), wide absorption in the area of a couple of eV. This relates to the inter band transition from valence bands to conduction. Numerous unique and real optical spectra of both metallic and semi-directing layer componds are clarified plainly in Wilson and yoffels article (1969). Later work on the gathering V metallic mixes is found in tile paper by Real (1976)

3.1 Computational details

The crystal of $\mathbf{Ta_{x}Nb_{1-x}s}$ in orthorhombic structure have space group *pmmm (No. 47).* The structure of unit and molecule of $\mathbf{Ta_{x}Nb_{1-x}s}$ is shown in Fig. 1. We used the full-potential linearized augmented plane-wave method (FPLAPW) as implemented in WIEN2K [33]. Our calculation were carried out by local density approximations (LDAs) [34], generalized gradient approximations (GGAs) [35], and Engel-Vosko GGA (EVGGA) [36] exchange-correlation potential. As the product of the smallest atomic sphere radius times the magnitude of the largest reciprocal-lattice vector (RMT_{min}, K_{max}), is known as plane-wave cutoff, which is 7 in our case. By minimizing the forces acting on the atoms atomic position of $\mathbf{Ta_{x}Nb_{1-x}s}$ compound were optimized. The self consistent calculations were converge when the difference in the total energy of the crystal did not exceed 0.01 mRy and the atomic forces did not exceed 1 mRy/a.u. By using densities of states (DOSs) hybridization effects were analyzed and some characteristics of inter-atomic bonding picture were visualized by means of charge density maps Table 1.

The calculation of optical properties requires a dense mesh of uniformly distributed K-points, the Brillouin zone integration was performed by using the tetrahedron method with 500 k-points in the irreducible part of the Brillouin zone. The optical response of the medium id describe by dielectric function at all photon energies.

There are two contributions of dielectric function in metals, arising from interband and intraband transitions and both involve phonon in order to account for the momentum transfer. The intraband and indirect interband transition add smooth background to the spectra [14]. Therefore they have been neglected in this study. The calculated direct interband contribution to the imaginary part of the dielectric function, is calculated by summing transition from occupied to unoccupied state over the Brillouin zone, weighted with the appropriate matrix elements giving the probability for the transition.

3.2 Results and discussion

3.2.1 Electronic structure

The Fermi surfaces, electronic band structure, as well as total and site-projected *l*-decomposed densities of states (DOS) for the studying $\mathbf{Ta_xNb_{1-x}s}$ compound have been calculated at the equilibrium geometries. The calculated energy band structure with highly symmetry direction in the Brillouin zone and total densities of states (TDOS) are shown in Fig. 2 and 3. The conduction and valence bands overlap considerably around Fermi level. This suggests that compound $\mathbf{Ta_xNb_{1-x}s}$ would exhibits metallic conductivity. TDOS has a large finite vale at the Fermi level, which is equal to 28.76 and 22.76 states/eV unit cell for LDA, GGA, and EVGGA, respectively. Again, this finding confirms the metallicity of this material. This leads to the estimation of Summerfield constants of $\mathbf{Ta_xNb_{1-x}s}$ under the assumption of free electron model.

In Fig. 2 and 3 TDOS and PDOS projected on each atomic species are illustrated. The TDOS shows a lot of structures which can be understood more vividly by PDOS. These PDOS identify the angular momentum character of the various structure. In the energy range from -6.0 eV to 3.0 eV the O p and Co d states shows the main contribution to the DOS, together with a contribution from La/Ba s and Co s/p states. The states ranging from -18.0 eV to -16.0 eV, all species are contributing to the DOS, only La/Ba p states are responsible for the structure between -14.0 and -13eV. The DOS is made from electronic states of the Ba/Co s and LA/Ba d states with small contributions of Ba/La s states at high energy (7.0-12.0 eV).

Fig. 2 represents the near-Fermi band structure of $\mathbf{Ta_xNb_{1-x}s}$ with the selected high-symmetry lines within the first Brillouin zone of the tetragonal crystal. It is clear that Fermi level is crossed by Co 3d bands, that indicates that the electrical conductivity of this phase should be metallic. It is seen that electronic states crossing Fermi level are responsible for the Fermi surface structure and are considered as key quantities to grasp the electronic structure og any metallic material [39-43]. There are five bands which are 110, 111, 112, 113, and 114, across the E_F level. The Fermi surface structures resulting from these five bands are exhibits in Fig. 5a-e with the merged band shown in . %f. The near-Fermi bands illustrate a complicated mixed nature meanwhile with quasi-flat bands. A series of high dispersive bands intersects the Fermi level. These qualities yield a multi-sheet Fermi surface, which consists (Fig. 5) of two quasi-two-dimensional (2D) electron-like sheets in the corners of the Brillouin zone, and closed disconnected electron-like pockets instead cylinder-like hole-like sheets for 47 *pmmm* material. The various electrons in the system whose topologies are closely related to the transport features of materials, such as electrical conductivity [44, 45] are defines by Fermi level. The colors (red, yellow, cerulean and blue) of Fermi surface depict variations in the electron velocities that are proportional to the superconductivity of the material [46].

To understand the nature of chemical bonding for the inquiry of compound, contour of charge densities in (3 2 0) plane is displayed in Fig. 4. It is vivid that interaction occurs among constituting elements due to the fact that states are degenerate with both angular momentum and lattice site, and also due to the difference in electronegativity between the comprising elements. It is clear that the O-Co bond strength is much stronger, however there is also a weak interaction between la and Co atoms due to which they are disturbed on the charge density contour around each other. Some ionic character that are Ba and La atoms have ionic bond nature are noticed from charge density contour. The bonding character can also be described as a mixture of covalent-ionic and due to the d-resonance in the vicinity of the Fermi level, is partly metallic.

Optical Properties

Fig. 6 exhibits tha calculated real and imaginary parts of dielectric function for $\mathbf{Ta_xNb_{1-x}s}$ as a function of photon energy from 0.0 to 14.0 eV. The dielectric function spectra helps in accounting the optical transitions in $\mathbf{Ta_xNb_{1-x}s}$. The imaginary part of the dielectric fuction was calculated from direct interband transitions, as Fig. 6 shows there is prominent structure in the imaginary part of the dielectric function of the compound shows by a peak around 1.0 eV and other smaller humps that decrease in intensity with increase in energy. These structures about 1.0 eV are associated with direct interband transitions. Our results shows, the transitions origiante from the occupied Co d bands below the Fermi level to the unoccupied hybridized Co s/p states above E_F. It is seen that the real part of the dielectric function of compound has a maximum at less than 1.0 eV and then decreases sharply and passes through zero at about 0.18eV. This is due to strong interband transitions from deeper lying valence bands to unoccupied bands above the Fermi level.

Fig. 7a and b depicts real and imaginary parts of the optical conductivity, which is calculated from the dielectric function. In the spectral region 9.0 to 11.5 eV there are three maxima in the conductivity spectra that can be assigned to optical transitions from occupied Ba p states to unoccupied La d or Ba d states. The reflectivity spectrum shown in Fig. 7 c. It can be seen that the reflectivity is over 72% in this compound within the energy range studied. This shows that the material will serve as a good reflector. There is a steady decrease in the reflectivity of compound with increase in the energy to form a valley at 6.8 eV, then again the reflectivity increases.

3.3 Conclusions

We have carried out ab-initio calculation of electronic structure, charge density, Fermi surface and optical properties of **$Ta_xNb_{1-x}s$** compound using a full-potential linearized augmented plane-wave method within LDA, GGA and EVGGA schemes. We shown that structural parameters obtained after relaxation are in good agreement with the experimental data. The electronic structure of compound **$Ta_xNb_{1-x}s$** has metallic nature which allows to calculate Fermi surface. The analysis of charge densities contours untangled that the bonding character in these compounds may result as a mixture between covalent-ionic and metallic nature. We find more keenly the calculated optical properties through the calculated optical spectrum, the reflectivity and optical conductivity.