Elastic, Electronic, and Optical properties of NaSnX (X=Sb, Bi, As): First principle calculations

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Abstract. In the present work, the structural, mechanical, electronic and optical properties of NaSnX (X=Sb, B, As) compounds have been investigated by means of first principles calculations. The generalized gradient approximation has been used for modeling the exchange-correlation effects. It has been observed that the calculated lattice parameters are in good agreement with the experimental and theoretical lattice parameters. Bulk modulus, shear modulus, Young's modulus Poisson's ratio, sound velocities and the Debye temperatures using the calculated elastic constants for NaSnSb, NaSnBi and NaSnAs compounds have been obtained. The electronic band structure and the projected density of states corresponding to the electronic band structure have calculated and interpreted. The obtained electronic band structure for NaSnSb and NaSnBi compounds are metallic in nature, and the NaSnAs compound is also a narrow semiconductor. Based on the obtained electronic structures, we further calculated the frequency-dependent dielectric function, the energy-loss function, optical conductivity, and reflection along the x- and z- axes.

1. Introduction
The topological insulators (TI) have attracted a lot of attention since their theoretical discovery. The topological materials exhibit interesting paradoxes. The bulk and surface properties of these materials show different physical properties. The surface properties of these materials are different and they exhibit good conductive or superconducting properties. The finding of 2 and 3 dimensional TI materials and the use of these materials in different application areas have been the main target of the researchers [1-3]. The HgTe/CdTe quantum well was theoretically estimated as the first TI, and this estimate was confirmed by transport experiments. Later, the two-dimensional (2D) InAs / GaSb quantum well was theoretically discovered. Other 2D TI compounds such as the bismuth double layers and monolayer Bi\textsubscript{2}Br\textsubscript{4}, ZrTe\textsubscript{5} and HfTe\textsubscript{5} were discovered theoretically using first principle methods. Three-dimensional (3D) TIs were initially estimated at Bi\textsubscript{1-x}Sb\textsubscript{x} and then Bi\textsubscript{2}Se\textsubscript{3}, Bi\textsubscript{2}Te\textsubscript{3} and Sb\textsubscript{2}Te\textsubscript{3} compounds with larger band gaps from this material were estimated [3-14].

We have determined that there is not much work in our literature research about these compounds that exhibit interesting physical properties. Dai et al. [3], using the DFT-GGA approach, calculated the bulk and surface electronic band structure of NaSnX (X = Sb, Bi, As) compounds and tried to explain the topological properties of these compounds. Jia et al. [2] studied NaXBi (X = Sn, Pb) compounds both experimentally and theoretically. In theoretical studies, they investigated the presence of the topological phase and Rashba effect by calculating the electronic band structures of the NaXBi (X = Sn, Pb) compounds using the DFT approach, and examined the dynamic and thermal properties of these
compounds by phonon spectra and DFT calculations. Our aim in this study is to fill this emptiness by examining the mechanical and optical properties of NaSnX (X = Sb, Bi, As) compounds which have not been studied theoretically as far as we know.

2. Method of calculation

In all of our calculations that were performed using the ab-initio total-energy and molecular-dynamics program VASP (Vienna ab-initio simulation program) [15-18] that was developed within the density functional theory (DFT) [19], the exchange-correlation energy function is treated within the a spin polarized GGA (generalized gradient approximation) by the density functional of Perdew et al. [20]. The potentials used for the GGA calculations take into account the 2p6s1 valence electrons of each Na-, 4d10s5p2 valence electrons of each Sn-, 4d10s5p2 valence electrons of each Sb-, 5d10s26p3 valence electrons of each Bi-, and 3d10s4p3 valence electrons of each As-atoms. When including a plane-wave basis up to a kinetic-energy cutoff equal to 12.16 Ha for NaSnSb/NaSnAs and 15.31 Ha for NaSnBi, the properties investigated in this work are well converged. The Brillouin-zone integration was performed using special k points sampled within the Monkhorst-Pack scheme [21]. We found that a mesh of 8x8x3 k points for NaSnSb, 12x12x4 k points for NaSnBi and 9x9x3 k point for NaSnAs was required to describe the structural, mechanical, electronic, and optical properties. This k-point mesh guarantees a violation of charge neutrality less than 0.008e. Such a low value is a good indicator for an adequate convergence of the calculations.

3. Result and discussion

3.1 Structural properties

NaSnX compounds crystallize in a hexagonal structure with the space group P63mc (No = 186). The compounds have optimized using atomic positions and lattice parameters given in Ref.(3). The lattice parameters obtained as a result of the optimization are given in Table 1. The calculated lattice parameters are in good agreement with the experimental and theoretical lattice parameters given in Table 1.

| Material  | Reference        | a (Å)  | c (Å)  | V0 (Å³) |
|-----------|------------------|--------|--------|---------|
| NaSnSb    | Present          | 4.3608 | 11.8135| 194.56  |
|           | Experimental[3]  | 4.3610 | 11.8360| 194.94  |
| NaSnBi    | Present          | 4.4983 | 11.6911| 204.87  |
|           | Experimental [3] | 4.5000 | 11.6950| 205.10  |
| NaSnAs    | Present          | 4.0684 | 11.7676| 168.68  |
|           | Theory [3]       | 4.0010 | 11.7290| 162.60  |

3.2. Elastic Properties

The elastic constant of a crystal is a measure of the crystalline response to the external strain applied. We used the strain-stress method [22] to calculate the elastic constants of NaSnX compounds. The obtained elastic constants are given in Table 2. The calculated elastic constants provide the mechanical stability criteria [C11]>[C12], C44>0, (C11+2C12)>2C12,2C11>2C12]. [23,24]. The C11 and C33 elastic constants in hexagonal crystals show resistance to linear compression in the a- and c-directions. Considering the elastic constants C11 and C33, the calculated elastic constants in NaSnSb and NaSnBi compounds are C11>C33 and in NaSnAs compound is C33>C11. Therefore, NaSnSb and NaSnBi compounds are more highly compressible in the c-direction, whereas NaSnAs is more highly compressible in the a-direction.

| Material  | Reference | C11 (GPa) | C12 (GPa) | C13 (GPa) | C33 (GPa) | C44 (GPa) |
|-----------|-----------|-----------|-----------|-----------|-----------|-----------|
| NaSnSb    | Present   | 56.17     | 12.68     | 23.45     | 40.69     | 21.75     | 22.85     |
| NaSnBi    | Present   | 52.67     | 16.58     | 23.27     | 38.27     | 18.04     | 20.11     |
| NaSnAs    | Present   | 30.97     | 3.79      | 11.78     | 32.62     | 13.59     | 10.90     |
Using the calculated elastic constants, the bulk (B) and shear (G) moduli are obtained from the Voigt (V) -Reuss (R) -Hill (H) approximation [25-27]. Young's modulus, Poisson's ratio, sound velocities, and Debye's temperature are also calculated from obtained bulk and shear moduli. The results are given in Tables 3 and 4. The value of the Poisson’s ratio is always 0.1 for covalent materials and 0.25 for ionic materials [28-30]. For this reason, the ionic character from the obtained Poisson's ratio ($\nu$ = 0.25 for NaSnSb, $\nu$ = 0.27 for NaSnBi and $\nu$ = 0.22 for NaSnAs) for all three compounds is dominant in the atomic bonding. We cannot say that these materials are stiff when we consider the value of Young's modulus (46.30 GPa, 41.16 GPa, and 27.72 GPa for NaSnSb, NaSnBi, and NaSnAs compounds, respectively), which is a measure of stiffness. If the B/G ratio is less (high) than 1.75, a material is brittle (ductile) [31,32]. Therefore, NaSnSb and NaSnAs compounds are brittle while NaSnBi compound is ductile. The calculated Debye temperature value (210.7 K) for NaSnSb is higher than the calculated Debye temperature value (172.4 K) and (176.9 K) for NaSnBi and NaSnAs. Generally, the Debye temperature is small for soft materials and large for hard materials [33-35]. We can say that all three compounds are not hard materials, but the NaSnSb compound is harder than the NaSnBi and NaSnAs compounds.

| Material | Reference | B (GPa) | Bx (GPa) | Bh (GPa) | Gv (GPa) | Gr (GPa) | Gh (GPa) | E (GPa) | $\nu$ | B/G |
|----------|-----------|---------|----------|----------|----------|----------|----------|---------|------|------|
| NaSnSb   | Present   | 30.24   | 30.16    | 30.20    | 19.72    | 17.48    | 18.60    | 46.30   | 0.25 | 1.62 |
| NaSnBi   | Present   | 29.98   | 29.73    | 29.86    | 17.02    | 15.38    | 16.20    | 41.16   | 0.27 | 1.84 |
| NaSnAs   | Present   | 16.58   | 16.19    | 16.39    | 11.56    | 11.19    | 11.38    | 27.72   | 0.22 | 1.44 |

Table 3. The calculated isotropic bulk modulus (B, in GPa), shear modulus (G, in GPa), Young’s modulus (E, in GPa), Poisson’s ratio for NaSnX (X=Sb, Bi, As) compounds

| Material | Reference | $v_l$ (m/s) | $v_t$ (m/s) | $v_m$ (m/s) | $\theta_D$ (K) |
|----------|-----------|-------------|-------------|-------------|----------------|
| NaSnSb   | Present   | 2034        | 3497        | 2256        | 210.7          |
| NaSnBi   | Present   | 1688        | 3008        | 1879        | 172.4          |
| NaSnAs   | Present   | 1634        | 2720        | 1807        | 176.9          |

Table 4. The calculated sound velocities ($v_l$, $v_t$, $v_m$) and the Debye temperatures for NaSnX (X=Sb, Bi, As) compounds

3.3. Electronic properties

The electronic band structures of NaSnX (X = Sb, Bi, As) compounds along the high symmetry points in the k space have been calculated. The results are given in Fig. 1. As can be observed from the band structures, the NaSnSb and NaSnBi compounds are metallic but the NaSnAs compound is a narrow semiconductor with $E_g$ = 0.04 eV. In the electronic band structure of the NaSnAs compound, the maximum of the valence band is between the $\Gamma$-K points but close to the $\Gamma$ point while the minimum of the conduction band is between the $\Gamma$-M points but close to the $\Gamma$ point. The results obtained for NaSnSb and NaSnBi compounds in comparison with the theoretical values [2,3] are consistent with the theoretical results, but the obtained $E_g$ value for the narrow semiconductor NaSnAs compound is smaller than the theoretical value.

The projected density of states corresponding to the electronic band structure of all three compounds have also been calculated and given in Fig. 2. In the NaSnSb compound, it is understood that the bands between -25 and -24 eV are occupied by the Na p states, and the bands between -23 and -21 eV are occupied by the Sn d states. The bands between -11 and -9 eV are occupied by the Sb s and Sn s states (but the Sb s states are more dominant than the Sn s states) while the bands between -8 and -5 eV are occupied by the Sn s and Sb s states (but the Sn s states are more dominant than the Sb s states). The bands just above and below the fermi level are occupied by all three states. In the NaSnBi compound, the lowest valence bands are occupied by Na p states. the bands between -23 and -21 eV are occupied by the Sn d and Bi d states. The bands between -11 and -9 eV are occupied by the Sb s and Sn s states (but the Bi s states are more dominant than the Sn s states) while the bands between -8 and -5 eV are occupied by the Sn s and Bi s states (but the Sn s states are more dominant than the Sb s states).
bands just above and below the fermi level are occupied by all three states. In the NaSnAs compound, the lowest valence bands are occupied by Na p states. The bands between -23 and -21 eV are occupied by the Sn d. The bands between -11 and -9 eV are occupied by the As s and Sn s states (but the As s states are more dominant than the Sn s states) while the bands between -8 and -5 eV are occupied by the Sn s and As s states (but the Sn s states are more dominant than the Sb s states). The bands just above and below the Fermi level are occupied by all three states.

Figure 1. Energy band structures for NaSnSb, NaSnBi, and NaSnAs compounds

Figure 2. The projected density of states for NaSnSb, NaSnBi, and NaSnAs compounds

3.4. Optical properties
The optical spectra of NaSnX, which result from the band structure in Fig.1, are plotted in Fig. 3. More precisely, the real ($\varepsilon_1$) and imaginary parts ($\varepsilon_2$) of the dielectric function ($\varepsilon$) [36,37] are displayed for the x- and z-axis. Above ~2 eV they show more or less the same line-shape as the corresponding spectrum. The pronounced reflection peaks between $\hbar\omega = 2.0$ eV and 10 eV in Fig.4 still appear with almost the same intensity. However, the spectra for small photon energies $\hbar\omega < 1.5$ eV are totally different. The spectral weights are redistributed to guarantee the oscillator strength sum rule. An additional pronounced peak appears at $\hbar\omega \approx 10.5$ eV, whereas the imaginary parts approach a small
positive value for $\omega \rightarrow 0$. Both observations are consequences of the modified band structure. The additional peak is due to van Hove singularities in the joint density of states at the highest optical transition energies near H and L points. The low-energy behavior is instead dominated by the non-conical 3D Dirac cones (Table 5). For intermediate energies the structure of the energy loss spectra in Fig. 3 is due to the details of the band structure. However, the high-energy behavior of the loss functions is also influenced by the collective plasmonic excitations of the valence electron with approximate plasma frequencies $\omega$ and corresponding valence electron densities. According to the band structure in Figs. 1 and 2, the valence electrons can be grouped into such due to Na p, s and Sn d electrons. Since only the valence s and p electrons can be nearly treated as free electrons in the formula for the plasma frequency, two peaks in the loss spectrum near 10.6 eV (only p electrons) and 13. eV (s and p electrons) can be explained. Because of the stronger binding, the right effective mass of the X p-d electrons is larger than the free-electron mass. Consequently, two other structures near 12.5 and 15.1 eV may be related to collective excitations where the delectrons partially contribute. The pronounced peak around $\hbar \omega = 10.3$ eV can be explained by contributions from the lowest Na s and X p bands into higher-lying conduction bands with p character.

Table 5. Some of the principal features and singularities of the linear optical responses for NaSnSb, NaSnBi and NaSnAs

| Material | $\varepsilon_1(eV)$ | $d\varepsilon_1/dE<0$ | $d\varepsilon_1/dE>0$ | $\varepsilon_2(eV)$ | $L(eV)$ |
|----------|-----------------|-----------------|-----------------|-----------------|--------|
| NaSnSb   | $\varepsilon_1^x$ | 3.02            | 12.71           | $\varepsilon_2^x_{\text{max}}$ | 2.42   | L-X 13.32 |
|          | $\varepsilon_2^x$ | 4.84            | 12.71           | $\varepsilon_2^x_{\text{max}}$ | 4.24   | L-Z 13.31 |
| NaSnBi   | $\varepsilon_1^x$ | 2.76            | 11.06           | $\varepsilon_2^x_{\text{max}}$ | 2.07   | L-X 11.06 |
|          | $\varepsilon_2^x$ | 4.15            | 11.75           | $\varepsilon_2^x_{\text{max}}$ | 3.46   | L-Z 13.82 |
| NaSnAs   | $\varepsilon_1^x$ | 2.82            | 11.87           | $\varepsilon_2^x_{\text{max}}$ | 1.77   | L-X 13.34 |
|          | $\varepsilon_1^z$ | 3.67            | 12.85           | $\varepsilon_2^x_{\text{max}}$ | 3.06   | L-Z 13.34 |

Figure 3. The real ($\varepsilon_1$) and imaginary ($\varepsilon_2$) parts of the dielectric function ($\varepsilon$) and energy-loss function (L) along the x- and z- axes for a) NaSnSb, b) NaSnBi and c) NaSnAs

The real($\sigma_1$) and imaginary $\sigma(2)$ parts of optical conductivity ($\sigma = \sigma_1 + i\sigma_2$) are shown in Fig. 4 for the whole investigated spectral range. In inspecting the spectra of the real part of $\sigma$ first, we recognize a metallic-like contribution merging into a Drude-like resonance well below 2 eV. All other peaks above 2 eV dominate $\sigma_1$ in the investigated compounds. We have proposed to ascribe all of these absorption peaks to generic electronic interband transitions. Their resonance frequencies closely coincide indeed with the direct transition along the $\Gamma$-K-L directions in the reciprocal space, as predicted by band structure calculations. The main panel of Fig. 4 emphasizes $\sigma_1$ in the spectral range of relevance for the following discussion. Again, we can appreciate the narrow metallic contribution and the two of the dominant absorptions pointed out here in above. These data, supported by band structure calculations, indicate that the degeneracy at the Dirac points in NaSnX is lifted by additionality breaking the time-
reversal symmetry with a canted magnetic order of the $X$-atoms, resulting in the formation of Weyl nodes.

**Figure 4.** The real ($\sigma_1$) and imaginary $\sigma(2)$ parts of optical conductivity ($\sigma = \sigma_1 + i\sigma_2$) and reflection ($R$) along the x- and z- axes for a) NaSnSb, b) NaSnBi and c) NaSnAs

4. Conclusion

We have performed the structural, mechanical, electronic, and optical properties of the NaSnSb, NaSnBi and NaSnAs compounds using the density functional theory. The lattice parameters obtained as a result of the optimization are in good agreement with the experimental and theoretical lattice parameters. Considering the calculated elastic constants of $C_{11}$ and $C_{33}$, the NaSnSb-NaSnBi and NaSnAs compounds have a higher compressible in the c- and a-directions, respectively. From the calculated Young's modulus and Debye temperature values, it is concluded that these compounds are soft materials. The ionic character from obtained Poisson's ratio for all three compounds is dominant in the atomic bonding. The electronic band structures and the projected density of states corresponding to these band structure have been calculated. The NaSnSb and NaSnBi compounds are metallic in nature, but the NaSnAs compound is a narrow semiconductor. The real and imaginary parts of the dielectric function, energy-loss function, optical conductivity, and reflection for these compounds have been calculated and interpreted.

5. References

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