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First-principle calculations of the elastic properties of $A^{II}B^{IV}C_2^V$ semiconductors

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ABSTRACT

First-principle calculations of the elastic properties of $A^{II}B^{IV}C_2^V$ semiconductors have been performed using the plane wave pseudo-potential method within the local density approximation. The values of elastic stiffness constants C_{ij}, i.e., C_{11}, C_{33}, C_{44}, C_{66}, C_{12}, C_{13}; bulk modulus (B) and shear modulus (G) have been calculated. The Debye temperature (Θ_D), Young's modulus (Y), Poisson's ratio (υ), Zener anisotropic factor (A) and G/B ratio have also been estimated. The values of C_{ij} of $ZnSnAs_2$ have been calculated for the first time. The calculated values of these parameters are compared with the available experimental and theoretical values. Reasonably good agreement has been obtained between them.

1. Introduction

In the recent past, several attempts have been made to study the electronic, elastic and thermal properties of $A^{II}B^{IV}C_2^V$ (A^{II} = Zn, Cd; B^{IV} = Si, Ge, Sn; and C^V = P, As) semiconductors [1]. This is because of their technological applications in the areas of infrared light emitting diodes and detectors [2,3], tunable laser in IR region [4,5], CO_2 laser [6,7] and NLO devices [5,8]. The $ZnGeP_2$ is an excellent nonlinear optical material with high second harmonic generation coefficients $\chi^{(2)}$ (=159 pm/V) and figure of merit. It has better optical properties than $LiNbO_3$, a most commonly used NLO material nowadays and exhibits good transparency over 0.7–12 μm wavelength region. The $CdGeAs_2$ has even larger $\chi^{(2)}$ (=236 pm/V) and FOM with high birefringence to ensure phase matching interaction. The $CdSiAs_2$ and $ZnSiAs_2$ semiconductors are widely used in photovoltaic solar cells, light emitting devices and infrared detectors [1]. The $CdSiP_2$ is another NLO material of this group used in mid infrared region. Recently, new chalcopyrites of $A^{II}B^{IV}C_2^V$ family have been reported by replacing A^{II} (Zn, Cd) type atom with Be [9], Mg [9,10] and Mn [11] atoms. These magnetic materials also offer potential applications in spintronics and magnetically controllable NLO devices [11]. Among the large number of $A^{II}B^{IV}C_2^V$ chalcopyrites only a few of them have been exploited for linear and nonlinear applications. Other materials in this family might offer better linear and nonlinear properties. Therefore, it has been thought of interest to study the various elastic and thermal properties of these semiconductors.

In view of these application perspectives the various electronic and elastic properties of these chalcopyrites have been studied in detail, both experimentally and theoretically. The various difficulties associated with the experimental processes and their cost, as well as difficulties in obtaining accurate values of the physical properties, researchers moved to calculate the physical properties of these semiconductors through theoretical and simulation methods. Recent development in the ability of computational power and advancement in modeling using first-principle calculations within density functional theory (DFT) has made prediction of elastic properties easier and relatively more accurate. The density functional theory has been used to explain the structural, electronic and optical properties of II-IV-V_2 and I–III–VI_2 groups of semiconductors by several workers [12–14]. First-principle calculations have been carried out to describe the magnetic properties of Mn-doped II–IV–V_2 semiconductors [15] and electronic properties of II–IV–V_2 (II = Be, Mg, Zn,Cd; IV = Si, Ge, Sn; and V = P, As) semiconductors [9,16–17]. The full potential linear augmented plane wave plus local orbit (FP-LAPW + lo) method has been used to find out the reflectivity spectra of $ZnXP_2$ (X = Si, Ge, Sn) semiconductors [18], electronic properties of $ASiAs_2$ (A = Zn, Cd) compounds [19], and the effect of cations on band structure of $ZnGeAs_2$ pnictides [20]. Various experimental and theoretical approaches have been made to explain the electronic, optical and elastic properties of $ZnSiP_2$ semiconductor [1,21,22]. Kumar et al. [23–26] have explained the various electronic [23], elastic [24], thermal [25]

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and nonlinear [26] properties of ternary chalcopyrites using plasma oscillations theory of solids. Other workers [27–29] have proposed various empirical relations for calculating the elastic constants, energy gaps and electronic polarizability of different binary and ternary semiconductors. Recently, the authors [30] have used the first-principle calculations to simulate the electronic, optical and elastic properties of $ZnSiP_2$ semiconductor, which is a part of a large family $A^{II}B^{IV}C_2^V$ compounds. In this paper, the values of elastic constants C_{ij} of whole family of $A^{II}B^{IV}C_2^V$ compounds have been simulated using *ab initio* method within DFT using Cambridge Sequential Total Energy Package (CASTEP) software. The values of C_{ij} of $ZnSnAs_2$ semiconductor have been reported for the first time. The values of bulk modulus (B), shear modulus (G), Debye temperature (Θ_D), Young's modulus (Y), Poisson's ratio (υ), Zener anisotropic factor (A) and G/B ratio of these compounds have also been calculated. The calculated values of all parameters are in fair agreement with the available experimental values in few cases where the experiments are performed and the values reported by different workers.

2. Theory and computational details

The first-principle calculations have been performed to study the elastic properties of $A^{II}B^{IV}C_2^V$ semiconductors using plane wave pseudo-potential total energy method as implemented in the CASTEP simulation software [31]. The calculations are based on the local density approximation (LDA) with exchange correlation Ceperley–Alders potential [32] parameterized by Perdew–Zunger scheme [33], with Norm-conserving pseudo-potential [34] using plane wave basis set cut-off at 400 eV. The integrals over the Brillouin Zone are replaced by a sum on a Monkhorst–Pack grid of $3 \times 3 \times 4$ special k-points [35]. Convergence shows that the Brillouin Zone sampling and the kinetic energy cut-off are sufficient for crystal optimization. The optimized crystal structures have been determined using the Broyden–Fletcher–Goldfarb–Shenno (BFGS) minimization technique with total energy of 5×10^{-6} eV/atom, Hellmann– Feynman ionic force of 0.01 eV/Å, maximum stress of 0.02 GPa and maximum displacement of 5×10^{-4} Å. After the optimization of geometry, the relaxed structures have been used for calculating the elastic stiffness constants. The elastic constants have been determined from first-principle calculations by applying a set of given homogeneous deformations with a finite value of structural parameters.

3. Results and discussion

3.1. Geometry and structural details

The chalcopyrite structure has a body-centered tetragonal (bct) structure (space group $I\bar{4}2d$:# 122), which is closely related to that of sphalerite (zinc-blende) with a specific ordered arrangement of cations accompanied by two small tetragonal distortions. These distortions make the unit cell tetragonal with the c-axis about twice the a-axis of the zinc-blende-type unit cell. The first of these distortions called tetragonal distortion which is represented by the parameter c/a, where a is the lattice constant in the x or y direction and c in the z direction. The second distortion is called tetrahedral distortion which is represented by the internal structural parameter u and determines the position of the anions in its neighbor tetrahedron. In an ideal chalcopyrite lattice, which is derivative of the zinc-blende, $u = 0.25$ and $c/a = 2$. For real compounds of pnictide of II–IV–V_2 group, $u = 0.214$–0.304 and $c/a = 1.769$–2.016 [16]. The considered atomic positions of $A^{II}B^{IV}C_2^V$ are given as: A atoms are positioned at (0,0,0) sites, B atoms occupy (0.5,0.5,0) positions and C atoms in (u,0.25,0.125) sites. The lattice parameters (a,c) and distortion parameter (u) have been considered to built the crystal structures [9].

3.2. Elastic properties

The elastic properties of materials are important as they provide information about the interatomic potentials and correlate the various fundamental solid state phenomena such as interatomic bonding, equations of state, thermal expansion, Debye temperature and phonon spectra as well as specific heat capacity [36–38]. Elastic constants are defined by means of a Taylor expansion of the total energy namely the derivative of the energy as a function of a lattice strain [33,39]. The tetragonal crystal has six independent elastic coefficients C_{ij}, i.e., C_{11}, C_{33}, C_{44}, C_{66}, C_{12} and C_{13}, and the cubic system has three independent elastic constants; C_{11}, C_{12} and C_{44}. The calculated values of the elastic constants C_{ij} of $A^{II}B^{IV}C_2^V$ semiconductors at 0 GPa are listed in Table 1 along with the available experimental and reported values. Table 1 shows that the elastic constants $(C_{11} = C_{22}) > C_{33}$, $C_{33} > (C_{44} = C_{55})$ and C_{66}, which shows that $A^{II}B^{IV}C_2^V$ semiconductors are mechanically anisotropic and stable at 0 GPa. The ratio of the elastic constants, $C_{11}/C_{33} = C_{12}/C_{13} = C_{44}/C_{66} \approx 1$ for all compounds, which further indicate that the elastic behavior of $A^{II}B^{IV}C_2^V$ chalcopyrites are pseudocubic in nature. The elastic constants also provide the information about the stability and stiffness of materials. For a stable tetragonal structure, the six independent elastic constants C_{ij} should satisfy the following Born–Huang criteria [43]:

$$C_{11} > 0, \quad C_{33} > 0, \quad C_{44} > 0, \quad C_{66} > 0 \tag{1}$$

$$(C_{11} - C_{22}) > 0, \quad (C_{11} + C_{33} - 2C_{13}) > 0 \tag{2}$$

$$[2(C_{11} + C_{12}) + C_{33} + 4C_{13}] > 0 \tag{3}$$

The values of Young's modulus Y, Poisson's ratio υ, and Zener anisotropic factor A of $A^{II}B^{IV}C_2^V$ semiconductors have also been calculated using the relations:

$$Y = \frac{9GB}{G + 3B} \tag{4}$$

$$\upsilon = \frac{1}{2}\left[\frac{(3GB - 2)}{(3GB + 1)}\right] \tag{5}$$

and

$$A = \frac{2C_{44}}{C_{11} - C_{12}} \tag{6}$$

where B is the bulk modulus and G is the shear modulus, which are related to the elastic constants by the relation [12]:

$$B = \frac{(C_{11} + C_{12})C_{33} - 2C_{13}}{C_{11} + C_{12} + 2C_{33} + 4C_{13}^2} \tag{7}$$

$$G = (G_V + G_R)/2 \tag{8}$$

The Voigt's shear modulus (G_V) and the Reuss's shear modulus (G_R) both are related to the elastic constant by the relations proposed by Sun et al [43].

The knowledge of the Young's modulus, Poisson's ratio and Zener anisotropic factor are important for the industrial and technological applications. The Young's modulus provides information about the measure of the stiffness of the solids, i.e. the larger the value of Y, the stiffer is the material. The Poisson's ratio υ gives the information about the characteristics of the bonding forces. The values of υ are typically between 0.1 t and 0.25 for covalent materials and interatomic forces are non-central forces [46]. For ionic crystals, the lower and upper limits of υ are 0.25 and 0.5, respectively, and interatomic forces are central forces [47]. The