Structural and elastic properties of $BiOCu_{0.875}S$ with Cu vacancies : A First principles study

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Abstract:
The structural and elastic properties of $BiOCu_{0.875}S$ with Cu vacancies have been investigated by using the first-principles density functional theory within the generalized gradient approximation. Population analysis suggests that the chemical bonding in $BiOCu_{0.875}S$ has predominantly ionic character with mixed covalent−ionic character. Basic physical properties, such as lattice constant, elastic constants C_{ij}, bulk modulus B, shear modulus G, were calculated. The elastic modulus E and Poisson ratio ν the ratio B/G, shear anisotropy and elastic anisotropy β_c/β_a were also predicted. The results show that tetragonal phase $BiOCu_{0.875}S$ is mechanically stable and behaves in a ductile manner.

Key words: DFT, Supraconductor, $BiOCu_{0.875}S$, mechanical properties.

1. Introduction

The search for new materials with iron oxypnictides structures and similar chemical properties, but that contain no toxic Arsenic, has recently picked up. One alternative has been to look at the Cu related compound. Among them, unique optoelectronic properties have been reported [1] in layered oxy-chalcogenides [2,3]. The physical properties reported for BiOCu*S* are limited to the transport [4] and infrared optical properties [5] of the oxyselenide BiOCuS. Theoretical studies made on the electron band structure of BiOCuS as a parent phase have shown that superconductivity can be achieved via appropriate doping [6]. Very recently, Cu deficient tetragonal $BiOCu_{1-x}S$ has been reported as a new superconducting compound having the Fe oxypnictide related structure [7]. However, superconductivity appears in some but not all of the BiOCuS compounds fabricated using different routes [8]. It is now believed

that the copper atomic deficiency play a key role in supporting superconductivity in this class of materials. Few months ago, L. Ortenzi *et.al.* [9] published their theoretical results and claimed that in doped $BiOCu_{1-x}S$ electron-phonon coupling is very strong and drives superconductivity while A. Ubaldini reported superconductivity in doped $BiOCu_{1-x}S$ and attributed to spin fluctuations as the pair mechanism.

To the best of our knowledge, there are no reports on the elastic properties of $BiOCu_{1-x}S$. However, it is important for fundamental physics and potential applications to study elastic properties of $BiOCu_{1-x}S$. Elastic properties provide information on interatomic potentials, interatomic bonding, equations of state, phonon spectra, specific heat capacity, thermal expansion, Debye temperature , etc [10] . In addition , elastic properties are essential for many practical applications related to the mechanical properties of solid: load deflection, internal strain, thermo-elastic stress, sound velocities and fracture toughness [10]. In this study, the chemical bonding and elastic properties of the tetragonal phase of $BiOCu_{0.875}S$ were studied using first-principles calculations based on DFT.

2. Method of calculation

2.1 Total energy electronic structure calculations

In the present electronic structure calculation, we apply the GGA for the exchange-correlation functional in the scheme of (PW91) [11] functions as implemented in the CASTEP code [12] . In order to study the fractional Cu vacancy in BiOCuS, we considered a cell larger than the basic unit. Thus we constructed a 2×2×1 super-cell consisting of 64 atoms (8 Bi;8 O, 8 Cu and 8S) . A plane-wave basis set with energy cut-off 650 eV is applied. Pseudo atomic calculations are performed for Bi, O, Cu and S atoms. The Bi $6s^2 6p^3$ electrons, O $2s^2 2p^4$ electrons, Cu $3d^{10} 4s^1$ electrons, and S $3s^2 3p^4$ electrons were explicitly treated as valence electrons. For the Brillouin-zone sampling, we use the 10×10×5 Monkhorst-Pack mesh[13] , where the self-consistent convergence of the total energy is at 1.0×10^{-5} eV/Atom. The structures were optimized by the BFGS algorithm [14].

2.2. Elastic properties

Elastic properties are closely related to various fundamental solid state properties such as Debye temperature, thermal expansion, Gruneisen parameter, etc. Hence, elastic constants are essential for many technological applications. Usually, elastic constants are defined by means

of a Taylor expansion of the total energy $E(V, \delta)$ for the system with respect to a lattice strain δ of the primitive cell volume V. The energy of a strained system is expressed as follows [15]:

$$E(V,\delta) = E(V_0,0) + V_0\left(\sum_i \tau_i\xi_i\delta_i + \frac{1}{2}\sum_{ij} C_{ij}\,\delta_i\xi_i\delta_j\xi_j\right) \qquad (1)$$

where $E(V_0, 0)$ is the energy of unstrained system with equilibrium volume V_0, τ_i is an element in the stress tensor, ξ_i and ξ_j are factors to take care of Voigt index. There are six independent elastic constants for tetragonal structure, i.e., C_{11}, C_{12}, C_{13},C_{33}, C_{44}, and C_{66}.

For the tetragonal crystal, its mechanical stability requires that its independent elastic constants should satisfy the Born's stability criteria [16]:

$C_{ii} > 0$, i = 1 , 3 ,4 ,6 ; $C_{11}-C_{12}>0$

$C_{11}+C_{33}-2C_{13}>0$; $2(C_{11}+C_{12}) + C_{33} + 4C_{13} > 0$ (2)

From the independent elastic constants above, the theoretical elastic modulus can be obtained. There are two approximation methods to calculate the modulus, namely the Voigt and Reuss method. For the tetragonal crystal, the Voigt (B_V) and Reuss (B_R) bulk modulus are given by:

$$B_V = \frac{2}{9}(C_{11} + C_{12} + 2C_{13} + C_{33}/2) \qquad (3)$$

$$G_V = (M + 3C_{11} - 3C_{12} + 12C_{44} + 6C_{66})/30 \qquad (4)$$

$$B_R = \frac{C^2}{M} \qquad (5)$$

$$G_R = 15/\left[\frac{18B_V}{C^2} + \frac{6}{C_{11}-C_{12}} + \frac{6C_{66}+3C_{44}}{C_{44}C_{66}}\right] \qquad (6)$$

$$C^2 = (C_{11} + C_{12})C_{33} - 2C_{13}^2 \qquad (7)$$

$$M = (C_{11} + C_{12}) + 2C_{33} - 4C_{13} \qquad (8)$$

The arithmetic average of the Voigt and Reuss bounds is called the Voigt–Reuss–Hill (VRH) method. The VRH averages for bulk modulus (B) and shear modulus (G) are given by:

$$B_H = B = \frac{B_V+B_R}{2} \qquad (9)$$

$$G_H = G = \frac{G_V + G_R}{2} \quad (10)$$

The Young's modulus (E) and the Poisson's ratio (ν) are then calculated from these elastic constants using the following equations:

$$E = \frac{9BG}{3B+G} \quad (11)$$

$$\nu = \frac{3B-2G}{2(3B+G)} \quad (12)$$

3 Results and discussion

3.1 Structural properties

The crystal structure of the tetragonal phase of BiOCuS belongs to the space group P4/nmm, Z=2 (ZrCuSiAs type), where blocks [BiO] are sandwiched with [CuS] blocks as depicted in Fig. 1. There are four in equivalent atomic positions: Bi at 2c site (1/4, 1/4, z_{Bi}), O at 2a site (3/4, 1/4, 0), Cu at 2b site (3/4, 1/4, 1/2), and S at 2c site (1/4, 1/4, z_S) [17], where z_{Bi} and z_S are the internal coordinates of Bi and S, respectively. The experimental lattice parameters are a=b=3.8691 Å and c=8.5602 Å, and the internal coordinates of Bi and S, were reported as z_{Bi}=0.14829 and z_S=0.6710 [17], respectively.

At the first stage, the full structural optimization of this phase was performed both over the lattice parameters and the atomic positions including the internal coordinate z_{Bi} and z_S. The calculated optimization lattice parameters a, c, V and atomic coordinates compared with available experimental data [17] for $BiOCu_{1-x}S$ are summarized in Table 1, which shows that the calculated values of GGA calculation are in agreement with the experimental results. The differences between our values and the experimental data may be due to the use of an approximate DFT. It is well known that the GGA leads to volume slightly overestimated in relation to the experimental value.

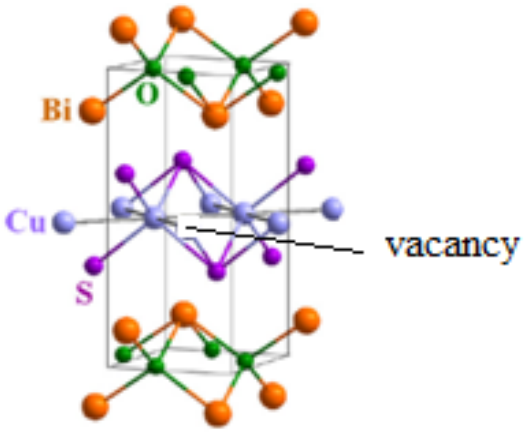

Fig. 1 Crystal structure of $BiOCu_{1-x}S$

Table 1 Calculated lattice parameters and atomic internal coordinate compared with available experimental data [17].

		a(°A)	c(°A)	V(A^3)	z_{Bi}	z_{Se}
$Bi_8O_8Cu_8S_8$	x=0	3.856	8.555	128.148	0.151	0.668
$Bi_8O_8Cu_7S_8$	x=0.125	3.827	8.542	127.925	0.147	0.667
Experimental[17]	x=0	3.869	8.560	128.145	0.148	0.671

3.2 Chemical bonding

The Mulliken bond population is useful for evaluating the bonding character in a material. A high value of the bond population indicates a covalent bond, and a low value indicates an ionic bond. Positive and negative values indicate bonding and anti-bonding states, respectively [18,19]. The Mulliken atomic population of $BiOCu_{0.875}S$ reported in Table 2 shows a significant charge transfer from [BiO] block to [CuS] blocks, indicating that the internal of [BiO] block and the [CuS] block is ionic character. The bond population reported in Table 3 shows that the intra-block of Bi−O and Cu−S is covalent character. The chemical bonding in $BiOCu_{1-x}S$ (x=0) has predominantly ionic character with mixed covalent−ionic character, which is in agreement with the results of Ref. [20].

Table 2 Mulliken atomic population of $BiOCu_{0.875}S$

	Population				
Species	s	p	d	Total	Charge/e
Bi	1.78	1.72	0.00	3.50	1.48
O	1.92	4.95	0.00	6.87	-0.86
Cu	0.56	0.81	9.77	11.04	-0.16
S	1.83	4.60	0.0	6.43	-0.43

Table 3 Mulliken bond population of $BiOCu_{0.875}S$

Bond	Population	Length (A)
Cu-Cu	0.46	2.732
O-O	-0.24	2.724
Bi-O	0.29	2.308
Cu-S	0.54	2.387

3.3 Elastic properties

To study the elastic properties of $BiOCu_{0.875}S$, the elastic constants C_{ij}, bulk modulus *B*, shear modulus *G*, Young's modulus *E*, and Poisson's ratio ν have been calculated for the first principle based on CASTEP code . The theoretical polycrystalline moduli for $BiOCu_{0.875}S$ may be computed from the set of independent elastic constants. Using the formulas: (3), (4), (5), (6), (7), (8), (9),(10),(11) and (12), the polycrystalline Young's modulus *E* (in GPa) and the Poisson's ratio ν are obtained and given in Table 4. From Table 4, we can see that these criteria (Eq. 2) are all satisfied, which indicates that $BiOCu_{0.875}S$ is mechanically stable.

The ductitle-brittle nature of materials can be discussed in terms of elastic constants of the relevant material. If the Cauchy's pressure (C_{12}-C_{44}) is negative (positive), the material is

expected to be brittle (ductile) [21]. In the present case this value is negative and it indicate that $BiOCu_{0.875}S$ is brittle. Another index of ductility is Pugh's ratio [22] and a material behaves in a ductile manner, if $G/B < 0.5$, otherwise it should be brittle. The critical number which separates the ductile and brittle was found to be 0.57 [23]. Thus the value of 0.456 for $BiOCu_{0.875}S$ thus indicates its brittle behavior. For LaOFeAs and LaOFeP, the values of G/B ratio are 0.574 and 0.704, respectively [24,25]. From the point of application, $BiOCu_{0.875}S$ is more readily machinable.

The elastic anisotropy of crystal, defined by the ratio $A = 2C_{44}/(C_{11} - C_{12})$ [26], yields a value of 0.768 for *A*. The factor $A = 1$ represents complete isotropy, while value smaller or greater than this measures the degree of anisotropy. Therefore, $BiOCu_{0.875}S$ shows strong anisotropic behavior. The parameter $\beta_c/\beta_a = (C_{11}+C_{12}-2C_{13})/(C_{33}-C_{13})$ expresses the ratio between linear compressibility coefficients of crystals [26]. From our data the value of β_c/β_a (= 1.516) indicates that the compressibility for $BiOCu_{0.875}S$ along *c* axis is greater than along *a* axis.

Table 4. Calculated elastic constants C_{ij} (GPa), bulk moduli *B* (GPa), shear moduli *G* (GPa), Young's moduli *E* (GPa), Poisson's ratio *v* , *A and* β_c/β_a for $BiOCu_{0.875}S$ at $T = 0$ K.

C_{11}	C_{12}	C_{13}	C_{33}	C_{44}	C_{66}	B	G	E	ν	A	*G*/*B*	β_c/β_a
150.22	62.05	55.25	122.54	33.84	48.45	84.4	38.52	102.55	0.282	0.768	0.456	1.516

4. Conclusions

1) The GGA calculated structural parameters of the tetragonal phase BiOCuS are in agreement with the experimental data.

2) The chemical bonding was analyzed, which shows that $BiOCu_{0.875}S$ has mainly ionic character with mixed covalent-ionic character.

3) The elastic constants were calculated and the bulks and shear modulus, elastic modulus, Poisson ratio were derived. All results show that $BiOCu_{0.875}S$ is mechanically stable and behaves in a ductile manner.

4) $BiOCu_{0.875}S$ shows strong anisotropic behavior.

5) From our data the value of β_c/β_a indicates that the compressibility for $BiOCu_{0.875}S$ along *c* axis is greater than along *a* axis.

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