

A density functional study of the electronic properties of bismuth subcarbonate $\text{Bi}_2\text{O}_2\text{CO}_3$



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ABSTRACT

Starting from the X-ray diffraction data of Huang et al. we have optimized the atomic positions by minimization of the forces (1 mRy/au) using Perdew–Burke–Ernzerhof generalized gradient approximation (GGA). From the relaxed geometry the electronic structure and the chemical bonding are determined. We have employed the full potential linear augmented plane wave (FP-LAPW) method as embodied in the WIEN2k code. In order to get a better estimate of the energy gap we have used the modified Becke–Johnson potential (mBJ) exchange–correlation potential. Our calculations show that the conduction band minimum (CBM) is situated at the centre of the Brillouin zone (BZ) and the valence band maximum (VBM) is located between W and T symmetry points of the BZ, indicating that bismuth subcarbonate is a semiconductor with an indirect band gap of about 0.8 eV. The electrons effective mass ratio (m_e^*/m_e) around Γ point are calculated. The partial density of states and the electronic charge density distribution shows that there exists a strong covalent bond between C and O atoms. Our calculated bond lengths and angles show very good agreement with the experimental data.

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1. Introduction

Bismutite have crystal structures typical of “Sillén” phases, and are closely related structurally to the only other Bi oxycarbonate mineral, kettnerite. Grice [1] has synthesized and refined bismuth subcarbonate $\text{Bi}_2\text{O}_2\text{CO}_3$ single crystals. Although the cell and the distribution of diffraction intensities obey tetragonal symmetry, attempts to solve the structure with tetragonal symmetry led to stereochemical problems. Greaves and Blower [2] have used powder neutron diffraction to investigate the structure of $\text{Bi}_2\text{O}_2\text{CO}_3$. They suggest that not all observed peaks could be indexed on the previously reported tetragonal unit cell, and a larger orthorhombic cell was adopted. Due to apparent orientational disorder of the CO_3^{2-} groups, the structure refinement was not totally satisfactory. $\text{Bi}_2\text{O}_2\text{CO}_3$ of small crystallite size decomposes at about 400 °C to β - Bi_2O_3 , which is thermodynamically unstable relative to α - Bi_2O_3 . They report that the structural relationships between $\text{Bi}_2\text{O}_2\text{CO}_3$ and

β - Bi_2O_3 as a means of rationalising this phenomenon. Liu et al. [3] synthesized $\text{Bi}_2\text{O}_2\text{CO}_3$ nanosheet with a thickness of less than 20 nm. They used the density functional theory (DFT) to calculate the electronic band structure and the density of states. Recently, Tian et al. [4] have synthesized $\text{Bi}_2\text{O}_2\text{CO}_3/\text{ZnWO}_4$ composite photocatalysts by a mixed calcination method after hydrothermal process. The catalysts were characterized by powder XRD, scanning electron microscopy, transmission electron microscopy, HRTEM, X-ray photoelectron spectroscopy (XPS), and UV–visible diffuse reflectance spectrum. They show that the hierarchical $\text{Bi}_2\text{O}_2\text{CO}_3/\text{ZnWO}_4$ nanocomposites were obtained by mixed grinding calcination method and $\text{Bi}_2\text{O}_2\text{CO}_3$ nanospheres grow on the primary ZnWO_4 particles. The resulting $\text{Bi}_2\text{O}_2\text{CO}_3/\text{ZnWO}_4$ composites show higher photocatalytic activities compared to pure ZnWO_4 and $\text{Bi}_2\text{O}_2\text{CO}_3$ particles under UV light irradiation. Cheng et al. [5] have used a facile, template free, and low temperature solution method to synthesize the hierarchical $\text{Bi}_2\text{O}_2\text{CO}_3$ flowerlike microstructures. The prepared $\text{Bi}_2\text{O}_2\text{CO}_3$ microflowers, with an average diameter of about 3 μm , and showed that these are composed of numerous 2-dimensional nanosheets with oriented terminal engagement. They employed UV/Vis spectroscopy to determine the band gap. In 2014, Huang et al. [6] have developed $\text{Bi}_2\text{O}_2\text{CO}_3$ as a novel nonlinear

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optical (NLO) material by the hydrothermal method. The developed $\text{Bi}_2\text{O}_2\text{CO}_3$ was characterized by X-ray diffraction (XRD), Fourier transform infrared (FTIR) spectra, high resolution transmission electron microscopy (HRTEM), UV–vis-NIR diffuse reflectance spectrum (DRS) and photoluminescence (PL) spectra. They found that the $\text{Bi}_2\text{O}_2\text{CO}_3$ crystallizes in the orthorhombic space group and it was constructed by $(\text{Bi}_2\text{O}_2)^{2+}$ layers and isolated $[\text{CO}_3]$ planar groups. The $(\text{Bi}_2\text{O}_2)^{2+}$ layers are always found in many Bi-based compounds with Aurivillius structure and Sillen structure [7,8]. In addition they investigated the PL properties of Eu^{3+} doped $\text{Bi}_2\text{O}_2\text{CO}_3$ under UV excitation. The obtained NLO efficiency was approximately 5 times as large as that of KDP (KH_2PO_4) standard.

To the best of our knowledge no comprehensive work neither experimental data nor first principles calculations on the electronic band structure, density of states and the electron charge density distribution of bismuth subcarbonate $\text{Bi}_2\text{O}_2\text{CO}_3$ have appeared in the literature. Therefore, we thought it would be worthwhile to perform such calculations using the full potential linear augmented plane wave (FP-LAPW) method within density functional theory (DFT) [9] which has been proved to be very accurate method [10,11] to investigate the electronic band structure, total and partial density of states and electronic charge density.

2. Details of calculation

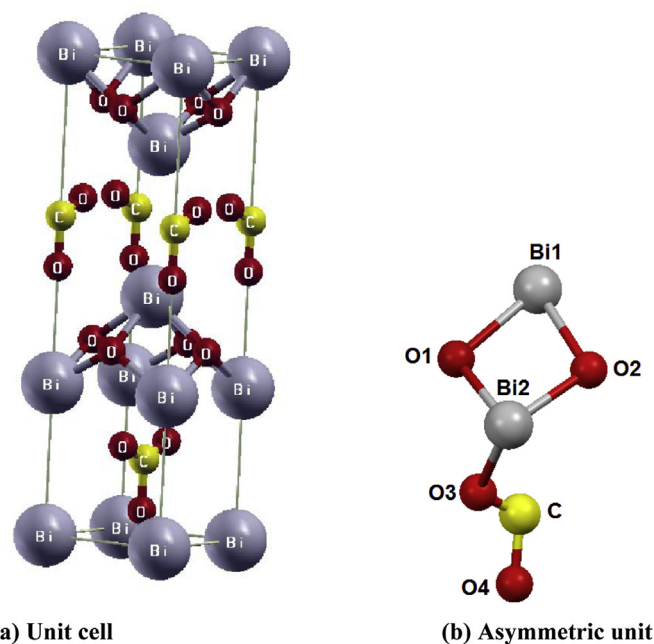
Bismuth subcarbonate $\text{Bi}_2\text{O}_2\text{CO}_3$ crystallizes in the orthorhombic space group $Imm2$ with lattice parameters $a = b = 3.8658$ (5) Å, $c = 13.6757$ (5) Å and $Z = 2$ [6]. The crystal structure is shown in Fig. 1(a) and (b). We have employed the full potential linear augmented plane wave (FP-LAPW) method in a scalar relativistic version as embodied in the WIEN2k code [12]. This is an implementation of DFT. Exchange and correlation potential is described by the modified Becke–Johnson potential (mBJ) [13], which optimizes the corresponding potential for electronic band structure calculations.

As starting point for our calculations, we have used the X-ray diffraction data taken from Huang et al. report [6]. Using the Perdew–Burke–Ernzerhof generalized gradient approximation (GGA) [14] we have optimized the atomic positions by minimization of the forces (1 mRy/au) acting on the atoms. The optimized atomic positions are compared with the experimental data [6] in Table 1. We find good agreement. From the relaxed geometry the electronic structure and the chemical bonding can be determined and various spectroscopic features can be calculated and compared with experimental data. Once the forces are minimized in this construction one can then find the self-consistent density at these positions by turning off the relaxations and driving the system to self-consistency. The Kohn–Sham equations are solved using a basis of linear APW's. The potential and charge density in the muffin-tin (MT) spheres are expanded in spherical harmonics with $l_{\text{max}} = 8$ and nonspherical components up to $l_{\text{max}} = 6$. In the interstitial region the potential and the charge density are represented by Fourier series. Self-consistency is obtained using 200 k points in the irreducible Brillouin zone (IBZ). We have calculated the electronic structure, total and partial density of states, and the electron charge density distribution using 500 k points in the IBZ.

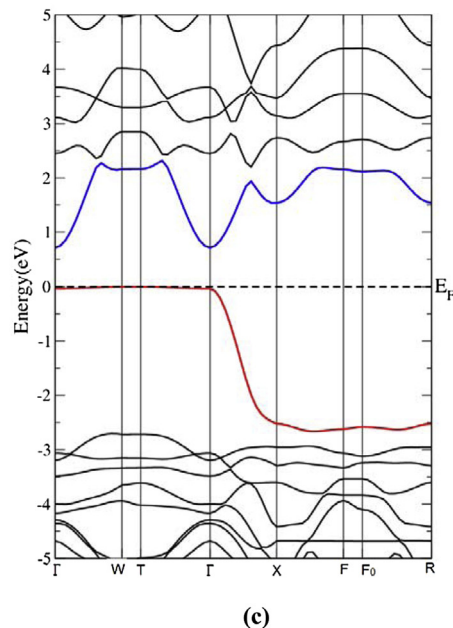
3. Results and discussion

3.1. Electronic band structure and density of states

The calculated electronic band structure of Bismuth subcarbonate $\text{Bi}_2\text{O}_2\text{CO}_3$ shows the conduction band minimum (CBM) is situated at the centre of the BZ and the valence band maximum (VBM) is located between W and T symmetry points of the BZ,



(a) Unit cell (b) Asymmetric unit



(c)

Fig. 1. (a) Crystal structure of bismuth subcarbonate $\text{Bi}_2\text{O}_2\text{CO}_3$ (unit cell); (b) Asymmetric unit; (c) Electronic band structure of bismuth subcarbonate $\text{Bi}_2\text{O}_2\text{CO}_3$.

suggesting that the investigated compound is an indirect band gap semiconductor, in agreement with the previous calculation [3] as illustrated in Fig. 1(c). The calculated energy band gap is about

Table 1
The optimized atomic positions in comparison with the experimental one [5].

Atoms	x-exp.	x-opt.	y-exp.	y-opt.	z-exp.	z-opt.
Bi1	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000
Bi2	0.5	0.5	0.5	0.5	0.18433	0.19157
C	0.00000	0.00000	0.00000	0.00000	0.33800	0.34775
O1	0.00000	0.00000	0.5	0.5	0.10400	0.09484
O2	0.5	0.5	0.00000	0.00000	0.10200	0.10059
O3	0.00000	0.00000	0.28600	0.25800	0.30500	0.29382
O4	0.00000	0.00000	0.00000	0.00000	0.44300	0.44224

0.8 eV (using mBJ) which much less than the experimental one (3.42 eV) [6]. This is attributed to the fact that the DFT calculations usually underestimate the energy band gap. However mBJ normally gives energy gaps that are in reasonable agreement with experiment. We feel that mBJ fails to do this for the present compound. To identify the contribution of each orbital in $\text{Bi}_2\text{O}_2\text{CO}_3$ atoms we investigate the angular momentum decomposition of the atoms projected density of states (PDOS) as represented in Fig. 2(a)–(e). As it is clear from Fig. 1(a) and (b) that there are three O atoms connected with C atom to form CO_3 group and two O atoms bonded with Bi atoms to form Bi_2O_2 group, therefore we will investigate the contribution of each O atom in CO_3 and Bi_2O_2 groups and hence in $\text{Bi}_2\text{O}_2\text{CO}_3$ compound. The lower conduction bands are formed mainly from Bi-5s/6p, O-2p, C-2p with negligible contribution from

Bi-5d/4f, C-2s and O-2s states. The upper valence bands are formed by O-2p, Bi-5s/6p, C-2s/2p with very small contributions of Bi-5d/4f and O-2s states. From the PDOS we can clarify the angular momentum character of the structures; the structure extended between -14.0 eV up to -7.0 eV is mainly originated from Bi-s, C-s/p with small contribution from Bi-6p and O-2s/2p states. In this energy region there exists a strong hybridization between Bi-5s, O-2p and C-2s/2p states. In the energy region from -7.0 eV up to Fermi level, a strong hybridization exists between O-2p and C-2s/2p states also between Bi-s and Bi-p states. From the CBM till 7.0 eV, O-p hybridize with C-2p state, from 7.0 eV and above there is a strong hybridization between Bi-5s/6p/5d/4f, C-2s/2p and O-2p states. The strong hybridization may leads to form a covalent bonding.

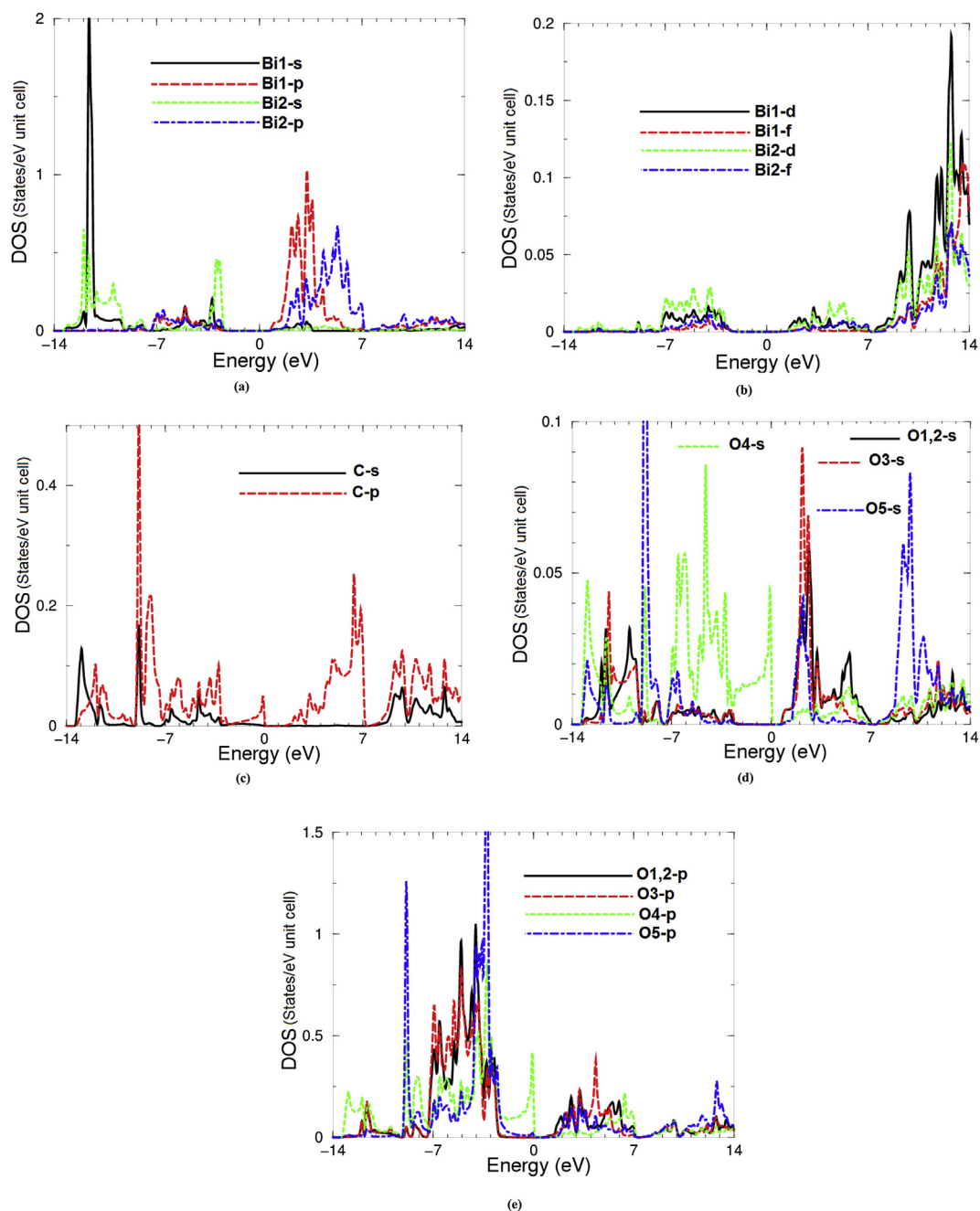


Fig. 2. Calculated partial density of states for bismuth subcarbonate $\text{Bi}_2\text{O}_2\text{CO}_3$; (a) partial density of states for Bi1,2-s/p; (b) partial density of states for Bi1,2-d/f; (c) partial density of states for C-s/p; (d) partial density of states for O1,2,3,4,5-s; (e) partial density of states for O1,2,3,4,5-p.

3.2. Electronic charge density distribution

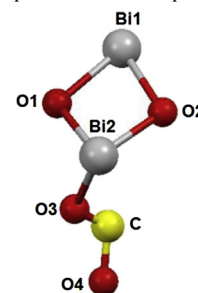
The electronic charge density distribution is a qualitative approach to investigating the interactions between the atoms. Therefore, we have investigated the electronic charge density in (1 0 1) crystallographic plane to describe the bonding properties of bismuth subcarbonate $\text{Bi}_2\text{O}_2\text{CO}_3$. Fig. 3(a) illustrated the electronic charge density contour in (1 0 1) crystallographic plane which represents all atoms. It is clear that Bi atom show strong ionic bonding and very weak covalent bonding with O atom, while O atom forms strong covalent bonding with C atom, depending on Pauling electro-negativity difference of Bi (2.02), C (2.55) and O (3.44) atoms. Since O atom possesses higher electro-negativity therefore it attracts the electrons. From the contour plot one can see that the majority of C and Bi electronic charge is transferred to O atom, as it is clear from Fig. 3(a) and (b) the O atoms surrounding by a circle of blue color which corresponds to the maximum charge (+1.0000) according to the thermal charge density scale. The charge around O atom is uniformly distributed. Also from the counter plots one can see the strong covalent bond between C and O atoms. In additional we have plotted (0–1 0) crystallographic plane which also represents all atoms (Fig. 3(b)). This plane confirms the covalent bonding between C–O atoms and the uniformly distributed charge around O atom. The selected bond lengths and angles are compared with experimental data [1] in Tables 2 and 3. We find good agreement.

3.3. Effective mass

In order to obtain accurate values of the electron effective mass one needs to calculate the curvature of the CBM in the vicinity of Γ point. The effective mass can be obtained using the definition of

Table 2

Selected bond lengths in comparison with the experimental data [1].



Bonds	Bond lengths Å (Exp.)	Bond lengths Å (this work)
Bi1–O1	2.40 (1)	2.41
Bi1–O2	2.39 (2)	2.40
Bi1–O4	2.842 (4)	2.91
Bi2–O1	2.22 (1)	2.19
Bi2–O2	2.23 (1)	2.24
Bi2–O3	2.67 (1)	2.68
C–O3	1.20 (2)	1.21
C–O4	1.42 (4)	1.41

effective mass as a second derivative of energy band with respect to the wave vector, k :

$$\frac{1}{m^*} = \frac{\partial^2 E(k)}{\hbar^2 \partial k^2} \quad (1)$$

Based on the calculated electronic band structures we have calculated the electron effective mass ratio (m_e^*/m_e) around Γ point the center of the BZ for the investigated compound. This value is

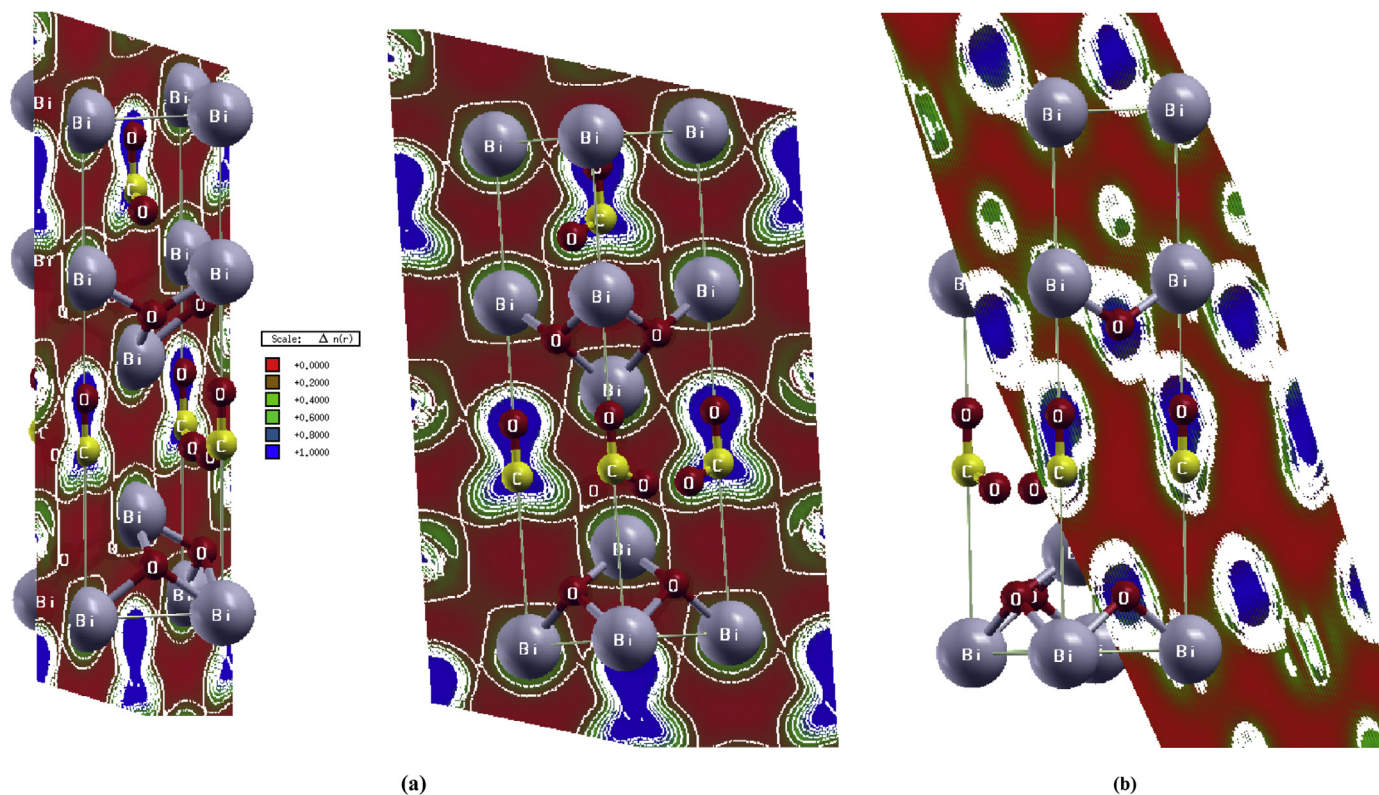
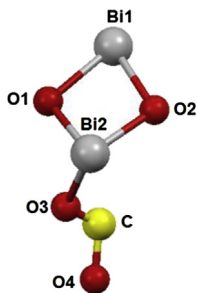


Fig. 3. Calculated electronic charge density counters; (a) illustrated the electronic charge density contour in (1 0 1) crystallographic plane which represents all atoms; (b) illustrated the electronic charge density contour in (0–1 0) crystallographic plane which represents all atoms.

Table 3
Selected bond angles in comparison with the experimental data [1].



Bonds	Bond angles (°) (Exp.)	Bond angles (°) (This work)
O3–C–O3	134 (4)	135.0
O3–C–O4	113 (2)	112.4

about 0.0019, we note that the electron effective mass for the CBM is very small because of the high curvature of the CBM around Γ , and this effective mass is isotropic so that the constant energy surfaces are spheres. For the VBM we expect large effective masses as the bands are flat over a wide range of symmetry directions.

4. Conclusions

The orthorhombic bismuth subcarbonate $\text{Bi}_2\text{O}_2\text{CO}_3$ with *Imm2* space group was investigated by means of the full potential linear augmented plane wave (FPLAPW) method within GGA and mBJ exchange correlation potentials. The calculated electronic band structure shows that the investigated compound is an indirect band semiconductor. The structure was optimized by minimization of the forces acting on the atoms. Based on the calculated electronic band structures we have calculated the electron effective mass ratio (m_e^*/m_e) around Γ point for the investigated compound. The partial

density of states show that there exists a strong hybridization between Bi-s/p/d/f, O-p and C-s/p states which may leads to covalent bonding, that confirm from the electronic charge density distribution contours in (1 0 1) and (0–1 0) crystallographic planes which exhibit a strong covalent bond between C and O atoms, while Bi atom show ionic bonding. Our calculated bond lengths and angles show very good agreement with the experimental data.

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References

- [1] J.D. Grice, *Can. Mineral.* 40 (2002) 693.
- [2] C. Greaves, S. K Blower, *Mater. Res. Bull.* 23 (1988) 1001.
- [3] Yuanyuan Liu, Zeyan Wang, Baibiao Huang, Kesong Yang, Xiaoyang Zhang, Xiaoyan Qin, Ying Dai, *Appl. Surf. Sci.* 257 (2010) 172–175.
- [4] N. Tian, H. Huang, Y. Zhang, Y. He, *J. Mater. Res.* 29 (2014) 641.
- [5] H. Cheng, B. Huang, K. Yang, Z. Wang, X. Qin, X. Zhang, Y. Dai, *Chem. Phys. Chem.* 11 (2010) 2167.
- [6] H. Huang, N. Tian, S. Jin, Y. Zhang, S. Wang, *Solid State Sci.* 30 (2014) 1.
- [7] C. Zhang, Y. Zhu, *Chem. Mater.* 17 (2005) 3537.
- [8] K.L. Zhang, C. M Liu, F. Q Huang, C. Zheng, W.D. Wang, *Appl. Catal. B* 68 (2006) 125.
- [9] P. Hohenberg, W. Kohn, *Phys. Rev. B* 136 (1964) 864.
- [10] Shiwu Gaom, *Comput. Phys. Commun.* 153 (2003) 190.
- [11] Karlheinz Schwarz, *J. Solid State Chem.* 176 (2003) 319.
- [12] P. Blaha, K. Schwarz, G.K.H. Madsen, D. Kvasnicka, J. Luitz, WIEN2k, an Augmented Plane Wave Plus Local Orbitals Program for Calculating Crystal Properties, Vienna University of Technology, Austria, 2001.
- [13] F. Tran, P. Blaha, *Phys. Rev. Lett.* 102 (2009) 226401.
- [14] J.P. Perdew, K. Burke, M. Ernzerhof, *Phys. Rev. Lett.* 77 (1996) 3865.