Available online at www.sciencedirect.com
ScienceDirect
Solid State Communications 146 (2008) 45–48
solid state communications
www.elsevier.com/locate/ssc

Ab initio study of *Cmca* phase of $Bi_{50}Sn_{50}$ ordered alloy

Bingbing Liu*

Department of Mathematics & Physics Science, Anqing Teacher College, Anqing, Anhui 246133, PR China

Received 11 December 2007; received in revised form 17 January 2008; accepted 19 January 2008 by E.V. Sampathkumaran
Available online 6 February 2008

Abstract

The geometrical structure, energetics and electronic properties of Cmca phase of $Bi_{50}Sn_{50}$ ordered alloy at 3 GPa were investigated using first-principle method, where two configurations were considered. The optimized structure parameters are consistent with the available experimental results. And it is found that the structure with Bi occupying 8d Wyckoff position is more preferable energetically and mechanically. The mechanical analysis suggests that the structure where Sn occupies 8d Wyckoff position is elastically unstable. For the structures considered, the corresponding total and partial electronic density of states were also discussed.

PACS: 61.50.Ah; 61.66.Dk

Keywords: A. Ordered alloy; C. *Cmca* phase; D. Electronics properties

1. Introduction

The Bi–Sn alloy system is a classic binary eutectic system and is an exemplary system that exhibits limited solid solubility and no intermediate compounds at ambient conditions. Its phase diagram is very similar to that of the well known Pb–Sn system which is widely used in electrical applications. However, as a low melting alloy Bi–Sn alloys can be used in temperature overload devices where the Pb–Sn are not suitable [1,2]. In order to search for novel structures for the solid solution under high pressure, there have been considerable efforts contributed to the area [3–8]. And an unknown intermediate phase assigned to the *X* phase was found with a superconducting transition temperature T_c up to 7.4 K [6], confirmed by x-ray [5] and neutron diffraction techniques [7]. But it is difficult to solve the structure by quenching to ambient pressure. A recent study successfully implements an *in situ* observation of the partially site ordered phase for Bi–Sn alloy obtained by annealing at 150 °C under a pressure of 3 GPa and refined the structure in space group *Cmca* [1]. Up to this date, however, there is little, if any, known theoretical investigation on the system. In this study, we focus on the site preference for occupancy of Bi and Sn at different Wyckoff positions in the *Cmca* phase of $Bi_{50}Sn_{50}$ alloy using first-principle total energy calculations. This composition of the alloy is much more easily implemented and modeled in the practical quantum simulation, which is also close to that of the experimentally obtained $Bi_{0.6}Sn_{0.4}$ alloy. Furthermore, the corresponding energy and electronic structures of $Bi_{50}Sn_{50}$ alloy are also investigated in detail.

2. Computational method

The first-principle calculations were performed with CASTEP code (MS Modeling, Accelrys) based on the plane wave basis set [9], with the ultrasoft pseudopotential for electron–ion interaction and exchange correlation potential of Perdew et al. [10] in the generalized gradient approximation (GGA-PBE) for electron-electron interaction. Calculations were applied to an eight-atom primitive cell of *Cmca* phase under pressure of 3 GPa. Periodical boundary conditions were also imposed. The typical configurations for Bi and Sn are $6s^26p^2$ and $5s^25p^2$ in which the d electrons are treated as core electrons. For testing the accuracy, the inclusion of d electrons in the valence of Bi was also considered, which shows no noticeable improvement in the investigated properties in this work. One-electron valence states were expanded in a basis

* Tel.: +86 556 8724584; fax: +86 556 8724584.
E-mail address: lbb122400@gmail.com.

0038-1098/$ - see front matter © 2008 Elsevier Ltd. All rights reserved.
doi:10.1016/j.ssc.2008.01.029

of plane waves with the cutoff energy equal to 400 eV. The electronic wave functions were sampled on a $5 \times 5 \times 4$ mesh in the Brillouin zone of the primitive cell. Such parameters have been tested to be sufficient for convergence. During the structure optimization, the total energy is minimized varying cell shape and all internal coordinates of the atoms under the restriction of the given symmetry, with all forces on atoms converging to less than 0.01 eV/Å.

3. Results and discussion

The *Cmca* phase of $Bi_{50}Sn_{50}$ ordered alloy is isostructure with the recent solved high-pressure modification structures Cs–V an Si–VI (space group *Cmca*), which can be well defined by the lattice constants and two non-equivalent symmetric positions [11,12]. There are two formula units per conventional orthorhombic unit cell which consists of 16 atoms (oC 16 in Pearson notation)-occupying two different Wyckoff positions-one is the 8f position located at flat layers while the other is the 8d position located at alternately puckered nearly square layers along [001] direction [13]. In this study, we have examined two types (denoted as A and B types) of configurations for the *Cmca* phase to elucidate the site-ordering in the crystal structure as shown in Fig. 1. For A-type structure, Bi occupies 8d positions and Sn occupies 8f positions while for B-type structure Bi and Sn occupy 8f and 8d positions respectively.

Now, we consider the structures determined by the first-principles calculations. The structural parameters including lattice constants, atomic fractional coordinates and ratios (a/c, b/c) are listed in Table 1, together with experimental data. It can be clearly seen that the optimized ratios and fractional positions for both structures are very close to the known *Cmca* structures. It may be also interesting to compare the total energy considering the different site occupancy. In the two structures, the A-type structure is a little lower in crystal energy and thus should be more stable than the B-type with energy difference 0.031 eV/atom.

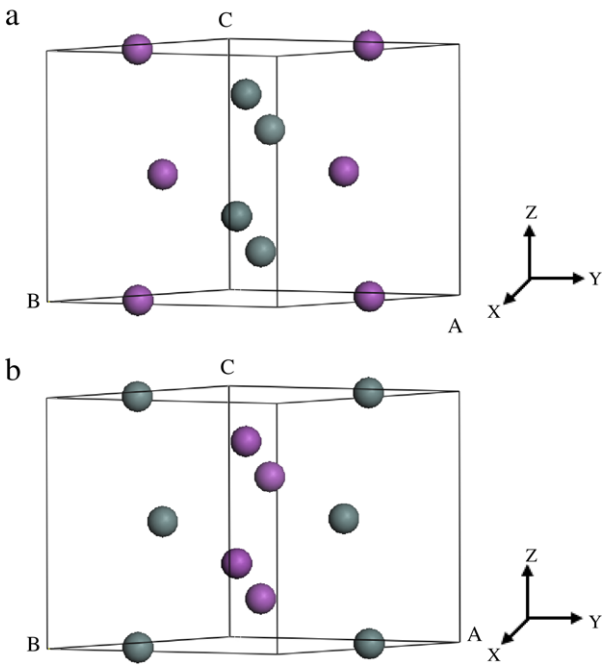

Fig. 1. Primitive cells of $Bi_{50}Sn_{50}$ *Cmca* phase: (a) A-type, (b) B-type. Bi and Sn are depicted in red and gray spheres. Four atoms in the center belong to 8f sites in the same flat plane, while the six atoms in the side are in 8d sites.

One condition for mechanical stability of a structure is that its strain energy must be positive against any homogeneous elastic deformation. For the orthorhombic structure, there are nine independent elastic stiffness constants: c_{11},c_{22}, c_{33}, c_{44}, c_{55}, c_{66}, c_{12}, c_{13}, and c_{23}. When all these elastic constants c_{ij} are larger than zero, the mechanical stability criteria for orthorhombic crystals [16] can be reduced to:

$$c_{11} + c_{22} - c_{12} > 0,$$
$$c_{11} + c_{33} - c_{23} > 0,$$
$$c_{22} + c_{33} - c_{23} > 0.$$

Table 1
Crystal data for *Cmca* phase of $Bi_{50}Sn_{50}$ ordered alloy with other available experimental results for comparison

Structure	A-type[a]	B-type[a]	Bi–IV[b,c]	Cs–V[d]	Si–VI[e]	$Bi_{40}Sn_{60}$[f]
Cell parameters (Å)						
a	10.496	10.396	11.121	11.205	8.024	10.735
b	6.228	6.221	6.580	6.626	4.796	6.327
c	6.137	6.219	6.580	6.595	4.776	6.312
Ratios						
a/c	1.710	1.672	1.690	1.699	1.680	1.701
b/c	1.015	1.001	∼1	1.005	1.004	1.002
Atomic coordinates						
x(8d)	0.209	0.217	0.216	0.216	0.218	0.212
y(8f)	0.158	0.167	0.173	0.173	0.173	0.167
z(8f)	0.322	0.316	0.327	0.327	0.328	0.334

[a] This work at 3 GPa.
[b] Ref. [14] and
[c] Ref. [15] at 3.9 GPa and 503 K.
[d] Ref. [11] at 12 GPa.
[e] Ref. [12] at 38.4 GPa.
[f] Ref. [1] at 5.8 GPa.

Table 2
The elastic-stiffness constants c_{ij}, bulk modulus B, and shear modulus G for $Bi_{50}Sn_{50}$ alloy in unit of GPa at 3 GPa

	c_{11}	c_{22}	c_{33}	c_{12}	c_{13}	c_{23}	c_{44}	c_{55}	c_{66}	B	G
A type	9	113	213	123	7	95	20	52	10	111	8
B type	43	139	53	87	27	21	24	−28	−41		

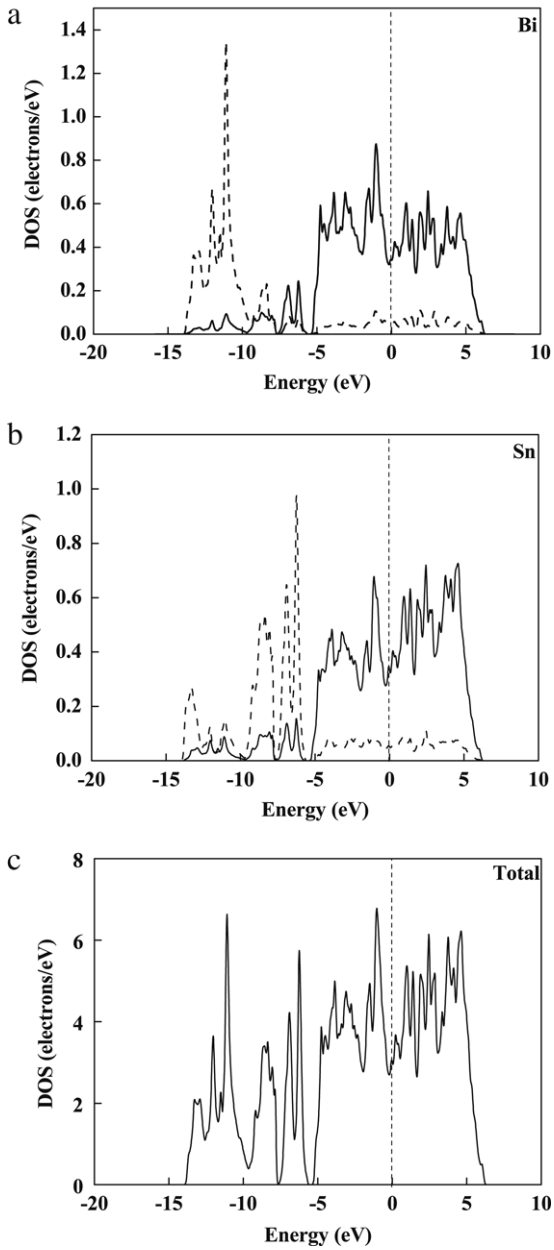

Fig. 2. Calculated partial DOS of Bi (a), Sn (b) and total DOS (c) for A-type structure in $Bi_{50}Sn_{50}$ Cmca phase. S and p orbits are represented by dash and solid lines respectively.

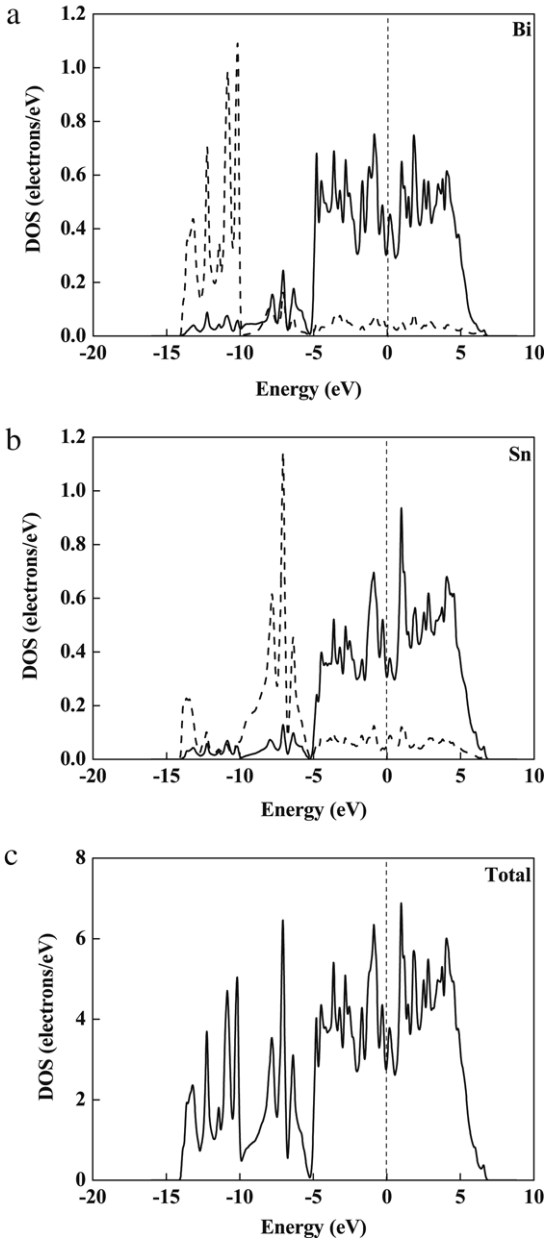

Fig. 3. Partial DOS of Bi (a), Sn (b) and total DOS (c) for B-type $Bi_{50}Sn_{50}$ Cmca phase, where S and p orbits are represented by dash and solid lines.

Nine stiffness constants evaluated for A and B types of $Bi_{50}Sn_{50}$ alloy are listed in Table 2, where the corresponding bulk modulus B, and shear modulus G are also given in terms of the Voigt scheme at 3 GPa. It can be easily seen that the elastic constants satisfy the above criteria for the A type $Bi_{50}Sn_{50}$ alloy. In contrast, the calculated elastic constants for the B type $Bi_{50}Sn_{50}$ alloy are suggestive of their mechanical instability. Therefore we only give the bulk and shear modulus of A type case: $B = 111$ GPa and $G = 8$ GPa, where low shear modulus indicates that it is easy to slip between adjacent atomic planes.

We also conducted the computation of the electronic structure of the $Bi_{50}Sn_{50}$ ordered alloy, which is important for understanding its intrinsic properties. The calculated total and site projected partial density of states for A- and B-type structures are displayed in Fig. 2 and Fig. 3. The total DOS

value for A-type structure at the Fermi level $N(E_F)$ that contributes much to the superconductivity [17] is very close to that of B-type with a value about 3.0 electrons/eV. For A-type structure, the energy bands between −5.5 and 6.3 eV originate dominantly from hybridization of Bi 6p with Sn 5p orbits which is not the case for Si–VI possessing essentially a sp-band nearly-free electron character [13]. The major contributions to valence bands (VBs) between −9.5 and −5.5 eV are from Sn 5s orbits, whereas VBs between −14 and −9.5 eV come mainly from Bi 6s orbits. This is also the similar case for B-type structure.

4. Conclusion

To conclude, we studied two configurations for *Cmca* phase of $Bi_{50}Sn_{50}$ ordered alloy at 3 GPa by the first-principle calculations. We have found that the structure in which Bi occupies 8d position and Sn occupies 8f position is energetically more stable with a very close DOS value at the Fermi level. Analysis of total and partial DOS spectra suggests that p orbits of Bi and Sn dominate the superconducting DOS value $N(E_F)$ for both A- and B-type structures.

References

[1] V.F. Degtyareva, O. Degtyareva, D.R. Allan, Phys. Rev. B 67 (2003) 212105.
[2] ASM metals handbook, Properties and Selection: Nonferrous and Special-Purpose Materials 2, 10th edition, ASM International, Metals Park, OH, 1992, 753.
[3] P.W. Bridgman, Proc. Am. Acad. Arts Sci. 82 (1953) 101.
[4] E.G. Ponyatovskii, Dokl. Acad. Nauk SSSR 159 (1964) 1342.
[5] D.E. Gordon, B.C. Deaton, Phys. Rev. B 172 (1972) 2982.
[6] A.G. Rabi'kin, V.N. Laukhin, Sov. Phys. JETP 34 (1972) 342.
[7] V.K. Fedotov, V.P. Zhebelev, E.G. Ponyatovskii, D.F. Litvin, Sov. Phys. Solid State 16 (1974) 2156.
[8] V.F. Degtyareva, I. Bdikin, S. Khasanov, Solid State Commun. 99 (1996) 907.
[9] M.D. Segall, P.L.D. Lindan, M.J. Probert, C.J. Pickard, P.J. Hasnip, S.J. Clark, M.C. Payne, J. Phys.: Cond. Matt. 14 (2002) 2717.
[10] J.P. Perdew, K. Burke, M. Ernzerhof, Phys. Rev. Lett. 77 (1996) 3865.
[11] U. Schwarz, K. Takemura, M. Hanfland, K. Syassen, Phys. Rev. Lett. 81 (1998) 2711.
[12] M. Hanfland, U. Schwarz, K. Syassen, K. Takemura, Phys. Rev. Lett. 82 (1999) 1197.
[13] U. Schwarz, K. Syassen, O. Jepsen, Solid State Commun. 113 (2000) 643.
[14] V.F. Degtyareva, Phys. Rev. B 62 (2000) 9.
[15] J.H. Chen, H. Iwasaki, T. Kikegawa, J. Phys. Chem. Solids 58 (1997) 247.
[16] Z.J. Wu, E.J. Zhao, H.P. Xiang, X.F. Hao, X.J. Liu, J. Meng, Phys. Rev. B 76 (2007) 054115.
[17] F.J. Ribeiro, M.L. Cohen, Phys. Rev. B 62 (2000) 11388.