Modifying structural polymorphs and tuning electronic properties in pressure-stabilized binary Ir–Sb phases

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The search for novel structures and chemical stoichiometry of binary Ir–Sb compounds is of great importance in view of their catalytic applications. Based on the results of swarm structure searching technique combined with density functional theory, we proposed the hitherto unknown Ir–Sb phase diagram in a wide pressure range with various chemical compositions. Besides two ambient pressure phases of IrSb3–Im3 and IrSb2–P21/c, five novel phases of IrSb–C2/c, IrSb–P1, IrSb2–P421m, IrSb2–I4/mmm and Ir2Sb–Pmmm were identified at high pressures. The phonon dispersion curves reveal that these phases are all dynamically stable. The calculated electronic results show that a mixed behavior of covalent, ionic and metallic bonds simultaneously exits in these novel phases. A pressure-induced electronic topological transition in Ir2Sb–Pmmm phase occurs according to the theoretical electronic band structures, while is not shown in other stoichiometries of the Ir–Sb system. Our work provides a potential opportunity for experimental synthesis of crystal structures with different chemical stoichiometries of the binary Ir–Sb system.

Introduction

Transition-metal compounds have aroused a great deal of interest from researchers due to their fundamental physics and as potential candidates for thermoelectric energy converters.1–4 Binary transition-metal antimonides are considered as important functional materials exhibiting a range of potential applications for superconductivity and as lithium ion battery anode materials.5–7 However, it is still a major challenge to experimentally synthesize transition-metal antimonides with novel structures and chemical stoichiometry in general under ambient conditions, because of the requirement for high temperatures and multi-step reactions under vacuum.8,9 Fortunately, recent studies experimental synthesis has made several successes to synthesize several transition-metal antimonides, e.g., arsenopyrite-type structure of CoSb2,10,11 skutterudite-type structure of CoSb3,12,13 nickel arsenide-type structure of NiSb and CoSb,14,15 marcasite-type structure of NiSb2,16 and anti-PbCl2-type structure of Cu3Sb.17

High temperature phase diagram of intermetallic compounds Ir–Sb was reported in the 1950s based on metallographic, thermal and X-ray analyses.18 The melting points were determined from cooling curves of alloys prepared from chemically pure components. Hexagonal NiAs-type IrSb was obtained according to metallographic observations of alloys after annealing 1500 K.19 The melting point of IrSb2 is higher than 1050 K, while IrSb3 forms by a peritectic reaction of 1126 K.20 Moreover, pressure induced irreversible isosymmetric transition of IrSb3 by the X-ray diffraction up to 43 GPa have been reported.21,22 Because of its relatively opened structure, it is expected to exhibit interesting behavior under high pressure. This void space can be filled with different atoms such as La or Ge to obtain the related family of compounds called filled skutterudites or stuffed skutterudites.23 Filled skutterudite compounds have been considered as potential candidates for thermoelectric applications.24,25 Interestingly, it could be interpreted as a pressure-induced self-insertion reaction which could be effectively improved the thermoelectric properties.

Utilizing the first-principle calculations combined with Boltzmann transport equation (BTE) and semiclassical analysis, high figure of merit zT’s of 1.45 are obtained in n-type doped IrSb3 at higher pressure.26 These studies show that pressure plays a powerful role to tune the thermoelectric properties.27 Thus, it is necessary to systematically investigate the crystal structure with various iridium antimonies stoichiometry and explore the corresponding bonding characterizes under high pressure.
In this paper, we have explored the binary Ir–Sb phase diagram via a first-principles swarm-intelligence structure search and established a comprehensive understanding of the evolution of its crystal structures at 0–100 GPa. In addition to reproducing the known IrSb-P6_{3}/mmc, IrSb_{2}-P2_{1}/c and IrSb_{1}-Im_{3}, the five novel high-pressure phases of IrSb-Pmmm, IrSb-C2/c, IrSb-P1, IrSb_{2}-P421m and IrSb_{2}-I4/mmm become energetically stable at 4.2 GPa, 16.4 GPa, 76.5 GPa, 45 GPa and 59.2 GPa, respectively. The electronic properties have been comprehensively investigated.\textsuperscript{28,29} Interestingly, pressure-driven evolution of the electronic topology transitions in IrSb_{2}-P4/mmm phase has been confirmed. Furthermore, the pressure-induced different bonding characters are shown in these antimonies. Our result represents a significant step toward understanding the structural and electrical behavior of the binary Ir–Sb system under extreme condition.

Results and discussion

We have performed systematic structure prediction for Ir–Sb system by variable-cell simulation with cell sizes of 1–4 formula units (f.u.) at 0–100 GPa. The crystal structure with the lowest energy was predicted under different pressures, and the enthalpies of formation for the iridium antimonies stoichiometry can be obtained in the structure search at varying pressures, as shown in Fig. 1. The relative thermodynamic stability of different Ir–Sb compounds with respect to elemental solids Ir and Sb is calculated according to the following equation: \( \Delta H_{f}(\text{IrSb}_{x}) = [H(\text{IrSb}_{x}) - xH(\text{Ir}) - yH(\text{Sb})]/(x + y) \). In the formula, \( H(\text{IrSb}_{x}) \) represents the enthalpy of the structure in the range of stable pressure, and \( H(\text{Ir}) \) and \( H(\text{Sb}) \) represent the enthalpy of the Ir atom and the Sb atom at the corresponding pressure. Then, we construct the convex hull data for Ir–Sb system at each pressure. Solid star indicates thermodynamically stable phases and the unstable or meta-stable phases are expressed by hollow star.

The built pressure-composition phase diagram of the Ir–Sb system is shown in Fig. 2, with the stable structures identified using colors and space groups. At ambient pressure, the already known stoichiometries of IrSb_{2}-Im_{3} and IrSb_{2}-P2_{1}/c are well-reproduced in our structural search calculations in Fig. 3(a) and (b). However, it is to be found that experimental phase of the ground state IrSb (space group P6_{3}/mmm) tend to decompose into IrSb_{2} phase in our pressure-composition phase diagram. Moreover, the optimized crystal parameters of IrSb_{2} (space group P2_{1}/c) are \( a = 6.734 \, \text{Å}, b = 6.675 \, \text{Å}, c = 6.831 \, \text{Å} \) in good well with the experimental values of \( a = 6.600 \, \text{Å}, b = 6.500 \, \text{Å}, c = 6.700 \, \text{Å} \), and that of in IrSb (space group P6_{3}/mmm) are \( a = b = 4.082 \, \text{Å}, c = 5.634 \, \text{Å} \) also consistent with the experimental values of \( a = b = 3.978 \, \text{Å}, c = 5.521 \, \text{Å} \), validating that our adopted structure searching method and PBE functional are applicable to the Ir–Sb system. No imaginary frequency is observed throughout the whole Brillouin zone, which indicates that the five novel phases are dynamically stable in the pressure region from this study, as shown in Fig. 4. The five novel phases of IrSb_{2}-P421m, IrSb_{2}-I4/mmm, IrSb_{2}-C2/c, IrSb-P1 and IrSb-Pmmm are stable shown in Fig. 3(c)–(g) under high pressure and the crystal structure and physical properties of these structures will be examined in detail next. IrSb_{3} is crystalized in a skutterudite-type structure, which can be also considered as a body centered cubic structure with a space group of Im_{3} in Fig. 3(a). The antimonies atoms form planer, rectangular Sb_{4} square with Sb–Sb distance of 3.033 Å. High-pressure calculations shows that the cubic IrSb_{3}-Im_{3} will be stability up to 22.2 GPa.

At ambient pressure, the IrSb_{2}-P2_{1}/c has a monoclinic symmetry in Fig. 3(b). Four Ir atoms and eight Sb atoms occupy the Wyckoff 4e site in the unit cell, respectively. In this structure, each Ir atom is coordinated to six Sb atoms in an octahedron environment, connected by an antimony bridge. The bond...
Fig. 3 Stable crystal structures of the considered Ir–Sb system for (a) Im3 structure of IrSb3, (b) P21/c structure of IrSb2, (c) P421m structure of IrSb2, (d) I4/mmm structure of IrSb2, (e) C2/c structure of IrSb, (f) P1 structure of IrSb and (g) Pmmn structure of Ir2Sb. The large (blue) and small (pink) spheres are Ir atom and Sb atom, respectively. The atomic positions are Ir at Wyckoff 8c (0.750, 0.250, 0.250) and Sb at 24g (0.500, 0.161, 0.346) for Im3; the atomic positions are Ir at Wyckoff 4e (0.229, –0.000, 0.790) and Sb at 4e (0.844, 0.863, 0.823) and 4e (0.351, 0.635, 0.878) for P21/c; the atomic positions are Ir at Wyckoff 4e (0.676, 0.824, 0.227) and Sb at 4e (0.778, 0.722, 0.606), 2a (0.000, 0.000, 0.000) and 2c (0.500, 0.000, 0.858) for P421m; the atomic positions are Ir at Wyckoff 2a (0.000, 0.000, 0.000) and Sb at 4e (0.500, 0.500, 0.151) for I4/mmm; the atomic positions are Ir at Wyckoff 8f (0.400, 0.673, 1.361) and Sb at 8f (0.000, 0.500, 0.152) for C2/c; the atomic positions are Ir at Wyckoff 2i (0.217, 0.525, 0.204) and 2i (0.676, 0.877, 0.183) and Sb at 2i (0.200, 0.032, 0.297) and 2i (0.722, 0.393, 0.289) for P1; the atomic positions are Ir at Wyckoff 2a (0.000, 0.000, 0.077), 2b (0.500, 0.000, 0.578) and 4e (0.000, 0.166, 0.612) and Sb at 4e (0.000, 0.350, 0.900) for Pmmn.

Fig. 4 Phonon-dispersion curves and PHDOS projected on Ir atoms and Sb atoms for (a) IrSb2-P421m at 45 GPa, (b) IrSb2-I4/mmm at 59.2 GPa, (c) IrSb-C2/c at 16.4 GPa, (d) IrSb-P1 at 76.5 GPa, and (e) Ir2Sb-Pmmn at 4.2 GPa.
length of Ir–Sb and Sb–Sb is 2.688 and 2.902 Å, respectively. At 45 GPa, the simulated IrSb2-P421m phase becomes more favorable, which has a tetragonal primitive symmetry with lattice parameters of $a = b = 5.854$ Å, and $c = 6.196$ Å in Fig. 3(c). In this case of the IrSb2-P421m phase, four Ir atoms occupy the Wyckoff 4e site and six Sb atoms lie in 4e, 2a, and 2c sites in the unit cell, respectively. Each Ir atom is coordinated to five Sb atoms to form a quadrangular pyramid. Interestingly, the antimony atoms consist of Sb3 units with the Sb–Sb distance of 2.782 Å, which join the neighbor six quadrangular together. In the IrSb2-I4/mmm phase, it has a tetragonal primitive symmetry, its equilibrium lattice parameters are $a = b = 2.955$ Å, and $c = 11.218$ Å at 59.2 GPa in Fig. 3(d). Two Ir atoms occupy the Wyckoff 2a site and four Sb atoms lie in 4e site in the unit cell. The IrSb2-I4/mmm phase consists of alternate Ir and Sb layers atoms, with the Sb–Sb distance of 2.955 Å in the square layer, which is larger than that of 2.782 Å in IrSb2-P421m.

The optimized structure of IrSb2-C2/c has a monochinic structure at 16.4 GPa. At pressure of 76.5 GPa, the IrSb2-C2/c transforms into an anorthic IrSb-P1 structure. In the IrSb2-C2/c phase, with lattice parameters of $a = 11.207$ Å, $b = 5.326$ Å, and $c = 5.061$ Å, and $\alpha = \gamma = 90.0^\circ$, $\beta = 110.7^\circ$ at 16.4 GPa in Fig. 3(e). Eight Ir atoms occupy the Wyckoff 8f site and eight Sb atoms lie in the 8f site in the unit cell. Each Ir atom is coordinated to five Sb atoms to form an octahedron in a unit cell. In the IrSb2-P1 phase, it belongs to a triclinic system, with lattice parameters of

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**Fig. 5** Electronic band structure and the PDOS on Ir atoms and Sb atoms for (a) IrSb2-P421m at 45 GPa, (b) IrSb2-I4/mmm at 59.2 GPa, (c) IrSb-C2/c at 16.4 GPa, (d) IrSb-P1 at 76.5 GPa, (e) Ir2Sb-Pmmm at 4.2 GPa, and (f) Ir2Sb-Pmmn at 8 GPa. Note that zero energy is at the Fermi level.
The metallic characters for the along high-symmetry directions in these structures. The results of 0.8.

Wycko structure, lattice parameters are IrSb-

low di

Ir 5d. The electrons transferred are responsible for the relatively below the Fermi level, indicating charge transfer from Sb 2p to

over, PDOS raises overlap between Sb 5p and Ir 5d orbitals (Fig. 5(a) localization function. As shown in the calculated PDOS structure, projected density of states (PDOS) and the electron

information of Ir–Sb system, the bond between Ir and Sb atom shows evident ionic character and a little covalent bond exists between Ir and Sb atoms at the same time.

It is worth noting that an electronic topological transition can occur at doping, high pressure, temperature or other external reagents alter the Fermi surface of an electronic system that has significant impacts on the corresponding physical and chemical properties.35,36 Therefore, we have checked the potential pressure-induced electronic topological transition in IrSb-Pmmm. As shown in Fig. 5(e), it is found that there is no band near the X point at 4.2 GPa. As the pressure increases, the
band moves down and approaches to the Fermi level at point X. Fig. 5(f) clearly shows that the red band along S–X–U is not fully occupied at 8 GPa and will form a hole pocket near the Fermi surface. Current theoretical predictions suggest that an electronic topological transition occurs in the \( \text{Ir}_2\text{Sb}\)-\( Pmmm \) structure.

In summary, the unbiased structure searching and density functional theory calculations are performed to explore the pressure-stabilized phases of \( \text{Ir–Sb} \) compounds under high pressure with a wide range of concentrations. Five novel phases of \( \text{IrSb}_2\)-\( P421m \), \( \text{IrSb}_2\)-\( Ia/mmm \), \( \text{IrSb}\)-\( C2/c \), \( \text{IrSb}\)-\( P1 \) and \( \text{Ir}_2\text{Sb\text{-}\( Pmmm \) were identified at high pressure. The theoretical phonon dispersion curves suggest that all these phases are dynamical stable. The calculated electronic band structures and density of states suggest that they are metallic. A pressure-induced electronic topological transition has been found in an \( \text{Ir}_2\text{Sb} \) phase. Accordingly, the electronic bonding states show evident covalent character in all of these five novel phases. The Bader charge analysis reveals that prominent electrons transfer from \( \text{Ir} \) to \( \text{Sb} \) atom in these novel phases are responsible for the ionic bonding feature of these compounds. The present findings establish the pressure-composition phase diagram of \( \text{Ir–Sb} \) system and corresponding electronic properties, which offer guidance for further fundamental understanding and experimental synthesis.

Methods

Structure prediction

Crystal structure prediction was performed at pressures of 0–100 GPa via an unbiased swarm intelligence based CALYPSO (Crystal structure AnaLysis by Particle Swarm Optimization) method,\textsuperscript{14–46} which was designed to search for the most stable or metastable structures of given compounds.\textsuperscript{37–41}

First-principles calculations

Structural optimizations, electronic structure and phonon calculations, and molecular dynamics were performed in the framework of density functional theory (DFT). The generalized gradient approximation (GGA) expressed by the Perdew–Burke–Ernzerhof (PBE) functional\textsuperscript{1} as implemented in the Vienna Ab initio Simulation Package (VASP)\textsuperscript{43,44} was adopted. The electron–ion interaction was described by the projector augmented-wave potentials, with \( 5d^76s^2 \) and \( 5s^25p^3 \) configurations treated as valence electrons for \( \text{Ir} \) and \( \text{Sb} \) atoms are, respectively. The cutoff energy of 600 eV and Monkhorst–Pack scheme with a \( k \)-point grid of \( 2\pi \times 0.03 \) Å\textsuperscript{-1} were adopted to obtain converged total energies (\( \sim \)1 meV per atom).\textsuperscript{45,46} Phonon dispersions were calculated using the supercell approach as implemented in PHONOPY code with a displacement of 0.01 Å for all calculation. \( 2 \times 2 \times 2, 4 \times 4 \times 1, 1 \times 2 \times 2, 2 \times 2 \times 2, \) and \( 3 \times 1 \times 1 \) supercells were found to be large enough for obtaining the converged dynamical matrices for the \( P421m \), \( Ia/mmm \), \( C2/c \), \( P1 \), and \( Pmmm \) structures, respectively.\textsuperscript{47} For both heavy elements of \( \text{Ir} \) and antimony-containing systems relativistic shifts in the electron’s atomic energy levels play a significant role.\textsuperscript{48} Therefore, the spin orbital coupling (SOC) effect has been considered for the calculations of electronic band structures.

Data availability

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Author contributions

Y. L. designed the research, S. L., D. Z. and Z. J. performed the calculations, Y. L., S. L., D. Z. and Z. J. analyzed the results and wrote the manuscript. All authors contributed to the discussions.

Conflicts of interest

The authors declare no competing financial or non-financial interests.

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References

1 S. T. Oyama, \textit{J. Solid State Chem.}, 1992, 96, 442–445.
2 G. D. Mahan, B. C. Sales and J. W. Sharp, \textit{Phys. Today}, 1997, 50, 42–47.
3 F. J. DiSalvo, \textit{Science}, 1999, 285, 703–706.
4 T. Caillat, A. Borschhevsky and J. P. Fleurial, \textit{AIP Conf. Proc.}, 1993, 271, 771–776.
5 G. A. Slack and V. G. Tsoukala, \textit{J. Appl. Phys.}, 1994, 76, 1665–1671.
6 N. N. Zhuravlev, G. S. Zhdanov and R. N. Kuz’min, \textit{Kristallografiya}, 1960, 5, 533–562.
7 A. Kjekshus and T. Rakke, \textit{Acta Chem. Scand., Ser. A}, 1977, 31, 517–529.
8 A. Kjekshus, \textit{Acta Chem. Scand.}, 1961, 15, 678–681.
9 F. Hulliger, \textit{Helv. Phys. Acta}, 1961, 34, 782–786.
10 G. S. Zhdanov and R. N. Kuz’min, \textit{Kristallografiya}, 1961, 6, 872–881.
11 T. Siegrist and F. Hulliger, \textit{J. Solid State Chem.}, 1986, 63, 23–30.
12 N. N. Zhuravlev and G. S. Zhdanov, \textit{Kristallografiya}, 1956, 1, 509–513.
13 K. Koga, K. Akai, K. Oshiro and M. Matsuura, \textit{20th ICT}, 2001, pp. 105–108.
14 U. Furst and F. Halla, \textit{Z. Phys. Chem.}, 1938, 40, 285–307.
15 T. Chen, J. C. Mikkelsen and G. B. Charlan, \textit{J. Cryst. Growth}, 1978, 43, 5–12.
16 A. Kjekshus, T. Rakke and A. F. Andresen, \textit{Acta Chem. Scand.}, 1974, 28, 996–1000.
17 M. Blander, G. Hagg and A. Westgren, Arkiv för kemi mineralogi och geologi B, 1935, 12, 1–6.
18 R. N. Kuz’min, G. S. Zhdanov and N. N. Zhuravlev, Kristallografiya, 1957, 2, 48–50.
19 R. N. Kuz’min, Kristallografiya, 1958, 3, 366–367.
20 H. Okamoto, J. Phase Equilib., 1994, 15, 640–642.
21 T. Caillat, A. Borschevsky and J. P. Fleurial, J. Alloys Compd., 1993, 199, 207–210.
22 H. Okamoto, J. Phase Equilib., 1994, 15, 567–568.
23 S. W. Kim, Y. Kimura and Y. Mishima, J. Electron. Mater., 2004, 33, 1156–1160.
24 G. S. Nolas, D. T. Morelli and T. M. Tritt, Annu. Rev. Mater. Sci., 1999, 29, 89–116.
25 G. Chen, M. S. Dresselhaus, G. Dresselhaus, J. P. Fleurial and T. Caillat, Int. Mater. Rev., 2003, 48, 45–66.
26 X. X. Yang, Z. H. Dai, Y. C. Zhao, W. C. Niu, J. Y. Liu and S. Meng, Phys. Chem. Chem. Phys., 2019, 21, 851–858.
27 S. Y. Lin, M. L. Xu, J. Hao, X. L. Wang, M. Wu, J. M. Shi, W. W. Cui, D. Liu, W. W. Lei and Y. W. Li, J. Mater. Chem. C, 2019, 7, 4527–4532.
28 C. Wang, Y. X. Liu, X. Chen, P. Lv, H. R. Sun and X. B. Liu, Chin. Phys. Lett., 2020, 37, 026201–026205.
29 S. Q. Jiang, X. Yang, X. L. Huang, Y. P. Huang, X. Li and T. Cui, Chin. Phys. Lett., 2020, 37, 016302–016306.
30 A. D. Becke and K. E. Edgecombe, J. Chem. Phys., 1990, 92, 5397–5403.
31 R. F. W. Bader, Acc. Chem. Res., 1985, 18, 9–15.
32 D. Zhou, Q. Li, Y. M. Ma, Q. L. Cui and C. F. Chen, J. Phys. Chem. C, 2013, 117, 12266–12271.
33 X. J. Ma, X. Li, D. Zhou, J. Xu, W. Q. Gao and Y. H. Liu, J. Alloys Compd., 2019, 791, 1257–1262.
34 Y. C. Wang, J. Lv, L. Zhu and Y. M. Ma, Comput. Phys. Commun., 2012, 183, 2063–2070.
35 Y. C. Wang, J. Lv, L. Zhu and Y. M. Ma, Phys. Rev. B: Condens. Matter Mater. Phys., 2010, 82, 094116–094124.
36 H. Wang, Y. C. Wang, J. Lv, Q. Li, L. J. Zhang and Y. M. Ma, Comput. Mater. Sci., 2016, 112, 406–415.
37 C. Y. Zhu, X. Qu, M. Zhang, J. Y. Wang, Q. Li, Y. Geng, Y. M. Ma and Z. M. Su, J. Mater. Chem. A, 2019, 7, 13356–13363.
38 G. T. Zhang, R. Gao, Y. R. Zhao, T. T. Bai and Y. F. Hu, J. Alloys Compd., 2017, 723, 802–810.
39 X. Q. Song, K. T. Yin, Y. C. Wang, A. Hermann, H. Y. Liu, J. Lv, Q. Li, C. F. Chen and Y. M. Ma, J. Phys. Chem. Lett., 2019, 10, 2761–2766.
40 Q. Li, D. Zhou, W. T. Zheng, Y. M. Ma and C. F. Chen, Phys. Rev. Lett., 2013, 110, 136403–136407.
41 D. Zhou, Q. Li, W. T. Zheng, Y. M. Ma and C. F. Chen, Phys. Chem. Chem. Phys., 2017, 19, 4560–4566.
42 J. P. Perdew, K. Burke and M. Ernzerhof, Phys. Rev. Lett., 1996, 77, 3865–3868.
43 G. Kresse and J. Hafner, Phys. Rev. B: Condens. Matter Mater. Phys., 1993, 47, 558–561.
44 G. Kresse and J. Hafner, Phys. Rev. B: Condens. Mater. Mater. Phys., 1994, 49, 14251–14269.
45 H. J. Monkhorst and J. D. Pack, Phys. Rev. B: Condens. Matter Mater. Phys., 1976, 13, 5188–5192.
46 D. Thirumalai, R. W. Hall and B. J. Berne, J. Chem. Phys., 1984, 81, 2523–2527.
47 A. Togo, F. Oba and I. Tanaka, Phys. Rev. B: Condens. Matter Mater. Phys., 2008, 78, 134106–134115.
48 G. Y. Gao, R. Hoffmann, N. W. Ashcroft, H. Y. Liu, A. Bergara and Y. M. Ma, Phys. Rev. B: Condens. Matter Mater. Phys., 2013, 88, 184104–184117.