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# Pressure-Stabilized Tin Selenide Phase with an Unexpected Stoichiometry and a Predicted Superconducting State at Low Temperatures

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Phys. Rev. Lett. **118**, 137002 — Published 28 March 2017

DOI: [10.1103/PhysRevLett.118.137002](https://doi.org/10.1103/PhysRevLett.118.137002)

# Pressure-stabilized tin-selenide phase with an unexpected stoichiometry and a predicted superconducting state at low temperatures

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(Dated: March 3, 2017)

Tin-selenium binary compounds are important semiconductors that have attracted much interest for thermoelectric and photovoltaic applications. As tin has a +2 or +4 oxidation state and selenium has an oxidation number of -2, only SnSe and SnSe<sub>2</sub> have been observed. In this work, we show that the chemical bonding between tin and selenium becomes counterintuitive under pressures. Combining evolutionary algorithms and density functional theory, a novel cubic tin-selenium compound with an unexpected stoichiometry 3 : 4 has been predicted and further synthesized in laser-heated diamond anvil cell experiments. Different from the conventional SnSe and SnSe<sub>2</sub> semiconductors, Sn<sub>3</sub>Se<sub>4</sub> is predicted to be metallic and exhibit a superconducting transition at low temperatures. Based on electron density and Bader charge analysis, we show that Sn<sub>3</sub>Se<sub>4</sub> has a mixed nature of chemical bonds. The successful synthesis of Sn<sub>3</sub>Se<sub>4</sub> paves the way for the discovery of other IV-VI compounds with non-conventional stoichiometries and novel properties.

Tin-selenium compounds are important semiconductors and widely applied in photovoltaics, thermoelectrics and memory-switching devices [1–3]. As tin has an oxidation state of +2 or +4 and selenium has a -2 oxidation number, the conventional binary compounds observed in the tin-selenium system are tin selenide (SnSe) and tin diselenide (SnSe<sub>2</sub>), which represent the typical stoichiometries in the IV-VI group. SnSe is a narrow band gap semiconductor with an unprecedented thermoelectric efficiency [4, 5]. It was shown that laminar SnSe (B16-type structure in the *Pnma* space group) undergoes a pressure-induced structural phase transition to the B33 structure (*Cmcm* space group) at about 10.5 GPa [6]. Under further compression, SnSe transforms to the B2 structure (*Pm* $\bar{3}$ *m* space group) and this phase was found to exhibit a superconducting transition at low temperatures above 58 GPa [7]. SnSe<sub>2</sub> is also a layered semiconductor with a hexagonal CdI<sub>2</sub>-type crystal structure (*P* $\bar{3}$ *m*1 space group) [8]. From X-ray diffraction (XRD), it was found that SnSe<sub>2</sub>, which is important for photoelectric applications [9], shows a second polytype with a space group of *R* $\bar{3}$ *m* [10]. On the other hand, the compound Sn<sub>2</sub>Se<sub>3</sub> has a controversial stoichiometry; it was argued that this compound is simply a superposition of SnSe and SnSe<sub>2</sub> [11].

Novel phases and compounds may be synthesized under high pressures [12, 13]. Theory-assisted material discovery based on ab initio evolutionary approach has been shown to be extremely effective [14–17]. Calcium carbides were investigated up to 100 GPa from first principles using the variable-composition evolutionary approach; two new compounds Ca<sub>2</sub>C and Ca<sub>2</sub>C<sub>3</sub> were predicted and successfully synthesized [18]. In the Zr-B binary system, Zr<sub>3</sub>B<sub>2</sub> and Zr<sub>2</sub>B<sub>3</sub> were predicted to be metastable below 50 GPa from the evolutionary approach [19]. Zhang *et al* predicted some unexpected sta-

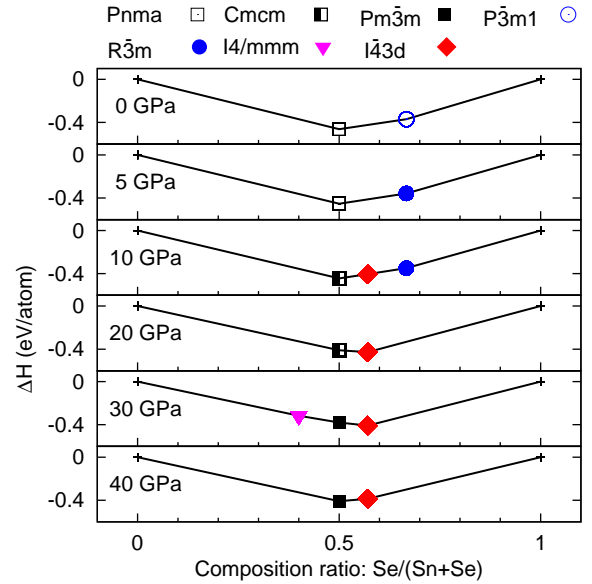


FIG. 1. Enthalpies of formation of the predicted stable compounds in the Sn-Se binary system. Solid lines represent the convex hulls at different hydrostatic pressures.

ble stoichiometries in the sodium-chlorine system under high pressures [20]. Drozdov *et al* recently observed a record high superconducting transition temperature in the sulfur-hydrogen system [21], in which the crystal structure of the new phase was firstly predicted from theory [22, 23].

Combining density functional theory (DFT) and evolutionary algorithms [24, 28], we carried out variable-composition structural searches in the Sn-Se system at pressures up to 40 GPa. A maximum number of 14 atoms is allowed in a unit cell in our calculations. High pressure-high temperature experiments were performed

to synthesize the predicted new compounds using commercial selenium powder (Alfa Aesar, 99.999%) and tin powder (Alfa Aesar, 99.995%) as reactants. A mixture of Sn and Se powder with a molar ratio of 3 : 4 was loaded into a diamond anvil cell equipped with 400  $\mu\text{m}$  culet diamonds and a stainless steel gasket. MgO was also loaded on the diamonds as the thermal isolator. The reactant mixture was compressed to 16.4 GPa and heated up to 1225 K using the on-line double-sided laser heating system at 16-IDB, Advanced Photon Source, and in situ powder X-ray diffraction was carried out simultaneously. The pressure was measured using the ruby fluorescence method [30]. The XRD data was collected using a PILATUS 1M detector and integrated using Dioptas [31].

It is seen from the convex hulls in Fig. 1 that there are two stable compounds, SnSe and SnSe<sub>2</sub>, being energetically preferable at low pressures. As expected, SnSe goes through a phase transition from the *Pnma* structure through *Cmcm* to a higher symmetry B2 structure with increasing pressure. The high-pressure crystal structures and the corresponding phase transition pressures are in good agreements with experimental observations [6, 7], indicating the reliability of our calculations. SnSe<sub>2</sub> has a CdI<sub>2</sub>-type structure with a space group of *P3m1* at 0 GPa, and it transforms to the *R3m* space group at 5 GPa. These two competing phases of SnSe<sub>2</sub> have very similar enthalpies at 0 GPa, e.g., *R3m* is only  $\sim 3.5$  meV/atom higher in enthalpy than *P3m1*, which may explain the experimental observations of different SnSe<sub>2</sub> polytypes. It is also noted that the convex hull at 20 GPa does not contain the 1 : 2 stoichiometry, indicating that SnSe<sub>2</sub> becomes unstable and decomposes at high pressures. On the other hand, a new compound with an unexpected stoichiometry 3 : 4 in the *I43d* space group is predicted to be energetically stable at 10 GPa. It is likely that SnSe<sub>2</sub> spontaneously decomposes to Sn<sub>3</sub>Se<sub>4</sub> and Se at high pressures. As can be seen from the convex hulls, Sn<sub>3</sub>Se<sub>4</sub> is energetically preferable up to the highest pressure considered in this work. The large pressure range where Sn<sub>3</sub>Se<sub>4</sub> is energetically preferable makes it possible to synthesize the compound. Unlike the layered crystal structures of SnSe and SnSe<sub>2</sub>, Sn<sub>3</sub>Se<sub>4</sub> has a more densely packed Th<sub>3</sub>P<sub>4</sub>-type crystal structure, which was mostly observed in compounds formed between rare earth and group IV, group V or group VI elements [32], or between transition metals (group IVB) and group V elements [33]. For the main-group binary compounds, only IV-V compounds were reported to have the Th<sub>3</sub>P<sub>4</sub>-type structure at high pressures [34]. Materials having this type of crystal structure were found to demonstrate great hardness, thermoelectricity, ferromagnetism or superconductivity [32, 35, 36]. In addition, a marginally stable Sn<sub>3</sub>Se<sub>2</sub> in the *I4/mmm* space group is observed at 30 GPa on the convex hull. However, the narrow pressure range where this compound exists makes it difficult to synthesize.

In addition to the energetics, we have studied the dy-

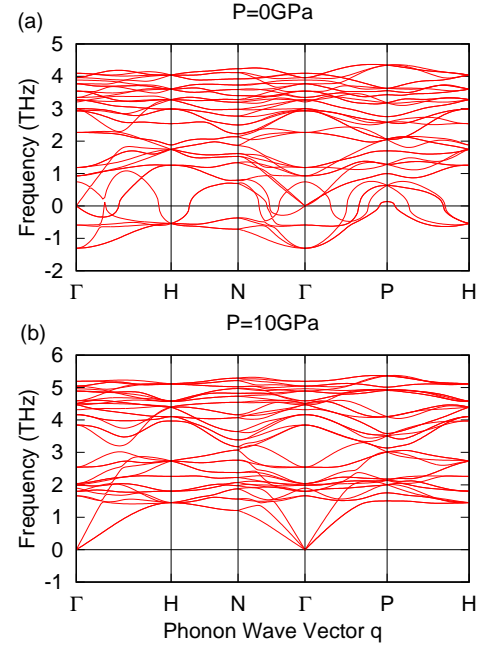


FIG. 2. Phonon dispersions of the predicted Sn<sub>3</sub>Se<sub>4</sub> compound at hydrostatic pressures of 0 GPa (a) and 10 GPa (b). The negative values represent imaginary phonon frequencies.

namical stability of Sn<sub>3</sub>Se<sub>4</sub> under high pressures [37]. Phonon dispersions have been calculated from first principles at  $T = 0$  K, as shown in Fig. 2. It is seen that Sn<sub>3</sub>Se<sub>4</sub> is dynamically unstable at 0 GPa due to the existence of large imaginary phonon frequencies. With increasing pressure, it is seen from Fig. 2(b) that the imaginary phonon modes are hardened, and the system becomes dynamically stable at 10 GPa. Based on the enthalpy and phonon calculations, it is predicted that Sn<sub>3</sub>Se<sub>4</sub> in the *I43d* space group is energetically and dynamically stable at pressures above 10 GPa.

To verify our prediction on the new compound, we performed corresponding high-pressure experiments. The synchrotron X-ray diffraction (XRD) patterns at approximately 16.4 GPa and 1225 K with Le Bail fitting are shown in Fig. 3. The wavelength of the incident X-ray is 0.4066 Å. The masked peaks (in gray) are from the thermal insulator MgO. It is seen that the predicted Sn<sub>3</sub>Se<sub>4</sub> phase can be clearly identified from the XRD patterns. The non-fitted peaks in the XRD patterns may be attributed to the formation of unidentified metastable phases in the experiment. The refined lattice parameter from the XRD data is  $a = 8.36$  Å and the space group is *I43d*. These experimental results are in excellent agreements with our calculations; the theoretical lattice parameter is 8.3 Å at 16 GPa and 0 K. The Sn<sub>3</sub>Se<sub>4</sub> phase still exists when the system is recovered to room temperature at about 16.4 GPa, whereas it becomes unstable and decomposes when the pressure is released. The experiment is consistent with our phonon calculations, where

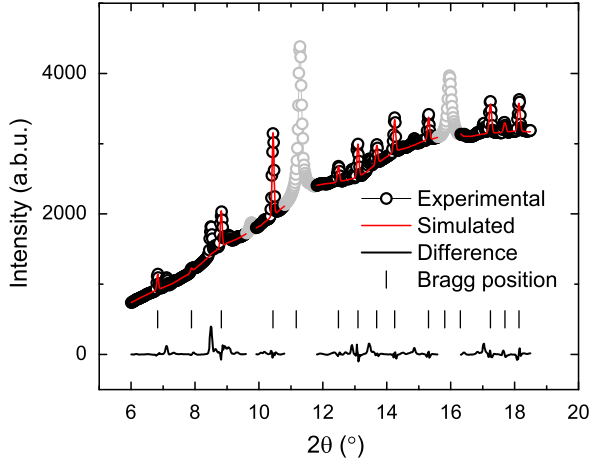


FIG. 3. Le Bail fitting plot of in-situ XRD patterns of  $\text{Sn}_3\text{Se}_4$  under 16.4 GPa and 1225 K. The experimental and simulated data is shown in black circles and red solid curves, respectively; their differences are shown in black solid curves and the Bragg positions are indicated by vertical bars. The peaks of MgO, the thermal isolator, are masked and shown in gray circles.

the imaginary phonon frequency of  $\text{Sn}_3\text{Se}_4$  indicates a dynamical instability at ambient condition.

After the successful synthesis of  $\text{Sn}_3\text{Se}_4$ , we have further calculated its electronic band structure and density of states (DOS) using the modified Becke-Johnson method [39], which gives more accurate band gap for SnSe [40]. As shown in Fig. 4(a), the band gap of SnSe is found to disappear at 10 GPa; a small overlap between the valence band maximum and the conduction band minimum is observed. The pseudogap at Fermi level indicates that SnSe exhibits a semimetallic behavior at 10 GPa, in agreement with previous study [41]. From the projected band structure and DOS, it is found that the electronic states below Fermi level are mainly contributed by the Se  $4p$  and Sn  $5s$  orbitals; above Fermi level, the main contribution comes from the Sn  $5p$  orbitals. For the new  $\text{Sn}_3\text{Se}_4$  compound (see Fig. 4(b)), a large DOS is observed at Fermi level, corresponding to a metallic state. In the vicinity of the Fermi level, majority of the electronic states originate from the Se  $4p$  and Sn  $5s$  orbitals. From the electronic structures of  $\text{SnSe}_2$  (see Fig. 4(c)), it is interesting that a band gap opens up at Fermi level, suggesting that  $\text{SnSe}_2$  is a semiconductor at 10 GPa with an indirect band gap of about 0.41 eV. The conduction band minimum is located in the  $F - P_1$  path, and the valence band maximum is in the  $Z - \Gamma$  path. The bottom of the conduction bands mainly contain the Se  $4p$  and Sn  $5s$  states, showing significant s-p hybridizations; the top of the valance bands are largely the Se  $4p$  states.

At high pressures above 58 GPa, SnSe was found to become a superconductor at temperatures below 4.5 K [7]. Comparing to SnSe,  $\text{Sn}_3\text{Se}_4$  has a much lower

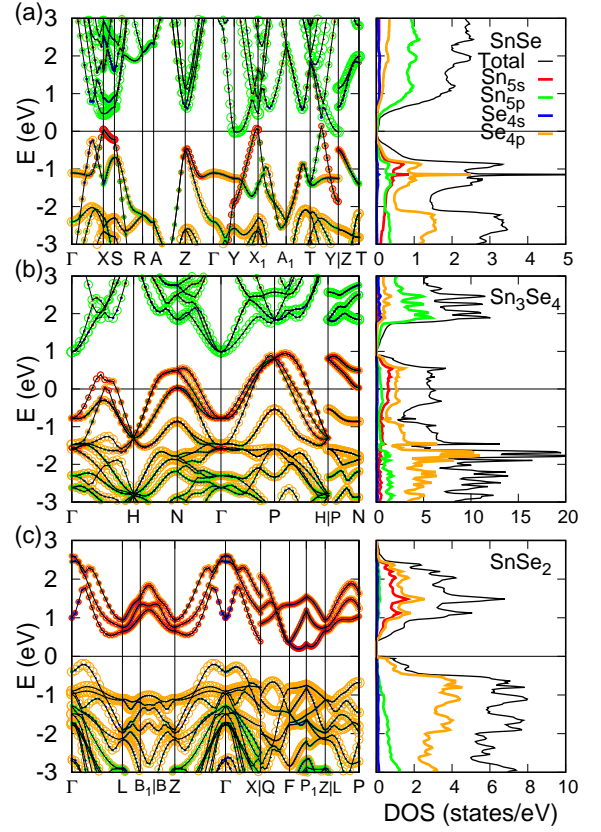


FIG. 4. Projected electronic band structures along high symmetry paths (left) and projected DOS (right) of SnSe (a),  $\text{Sn}_3\text{Se}_4$  (b) and  $\text{SnSe}_2$  (c) at 10 GPa. Fermi level is located at 0 eV. Different circle sizes correspond to the projected weights of different orbitals.

metallization pressure, suggesting a potential superconductive transition at lower pressures. Based on the electron-phonon coupling calculations, we have obtained the Eliashberg function at 10 GPa (see Fig. S1 in supplementary materials) [42]. Using the Allen-Dynes equation with typical values of the Coulomb pseudopotential  $\mu^*$  in between 0.1 and 0.14, the superconducting transition temperature of  $\text{Sn}_3\text{Se}_4$  is predicted to be in the range of 3.3-4.7 K at 10 GPa. Although the predicted  $T_c$  value needs further experimental verifications, the unexpected stoichiometry of  $\text{Sn}_3\text{Se}_4$  results in a superconducting state at a much lower pressure than previously believed for the Sn-Se binary system.

From the charge density shown in Fig. 5, it is seen that electrons tend to move away from Sn atoms and concentrate around Se atoms, which is consistent with their oxidation states. It is also seen that the charge distributions are obviously directional. Therefore, the chemical bonds in these compounds are expected to exhibit a mixed ionic and covalent character. Due to the layered crystal structures of SnSe and  $\text{SnSe}_2$ , strong chemical bonds exist in the inner layer directions. In SnSe, all of the Sn atoms or Se atoms are in equivalent lattice sites. Each Sn atom is



TABLE I. Bader charge analysis on different Sn-Se compounds at 10 GPa. Due to the very similar Bader charges of the non-equivalent Sn or Se atoms in  $\text{SnSe}_2$ , only the average values are shown.

	Sn (e)	Se (e)
$\text{SnSe}$	0.82	-0.82
$\text{Sn}_3\text{Se}_4$	0.94	-0.70
$\text{SnSe}_2$	1.15	-0.58

coordinated by one nearest neighbor Se atom ( $d_1 = 2.7$  Å) and four next-nearest neighbor Se atoms ( $d_2 = 2.9$  Å). Although  $d_1$  and  $d_2$  are rather similar, the charge density distributions between the nearest and the next-nearest neighbors are significantly different. There are two non-equivalent Sn lattice sites and three non-equivalent Se lattice sites in  $\text{SnSe}_2$ . Different Sn sites have the same amounts of nearest neighbor Se atoms ( $d_1 = 2.7$  Å) but different numbers of next-nearest neighbor Se atoms ( $d_2 > 4.0$  Å). As the next-nearest neighbor Se atoms are relatively far away, non-equivalent Sn atoms show similar electron density distributions. For the newly discovered  $\text{Sn}_3\text{Se}_4$ , all Sn or Se atoms are equivalent. Each Sn atom has four nearest neighbor ( $d_1 = 2.8$  Å) and four next-nearest neighbor ( $d_2 = 3.1$  Å) Se atoms. It is noted that the charge density in the interstitial sites of  $\text{Sn}_3\text{Se}_4$  is significantly higher than those in  $\text{SnSe}$  and  $\text{SnSe}_2$ . A more delocalized electron distribution in  $\text{Sn}_3\text{Se}_4$  is consistent with its metallic behavior.

As Sn atoms exhibit oxidation states of +2 or +4, and Se atoms have a -2 oxidation number, the existence of  $\text{SnSe}$  and  $\text{SnSe}_2$  is expected; nonetheless, the formation of  $\text{Sn}_3\text{Se}_4$  is counterintuitive. Bader charge analysis [46] has been performed to further investigate the charge transfer in these compounds. It is seen from TABLE I that the number of electrons which each Sn atom donates to Se increases from  $\text{SnSe}$  through  $\text{Sn}_3\text{Se}_4$  to  $\text{SnSe}_2$ . On the other hand, due to the increasing Se atomic percentage, the number of electrons which each Se atom accepts decreases. The electron transfers given by Bader charge analysis are significantly smaller than the standard oxidation numbers, which may be related to the mixed ionic and covalent bond characters as discussed in  $\text{SnSe}$  [47],  $\text{Pb}_{1-x}\text{Sn}_x\text{Se}$  [48] and the V-VI compounds [49].

In summary, we have performed systematic variable-composition evolutionary searches in the tin-selenium system under hydrostatic pressures up to 40 GPa. A new cubic compound  $\text{Sn}_3\text{Se}_4$  with an unusual stoichiometry is predicted to be stable above 10 GPa. Comparing to the layered crystal structures of  $\text{SnSe}$  and  $\text{SnSe}_2$ ,  $\text{Sn}_3\text{Se}_4$  is more densely packed. Our calculations have been verified by the successful synthesis of  $\text{Sn}_3\text{Se}_4$  in a diamond anvil cell. From synchrotron X-ray diffraction, the space group and the lattice constant are determined and they are in agreement with our theoretical results. Electronic

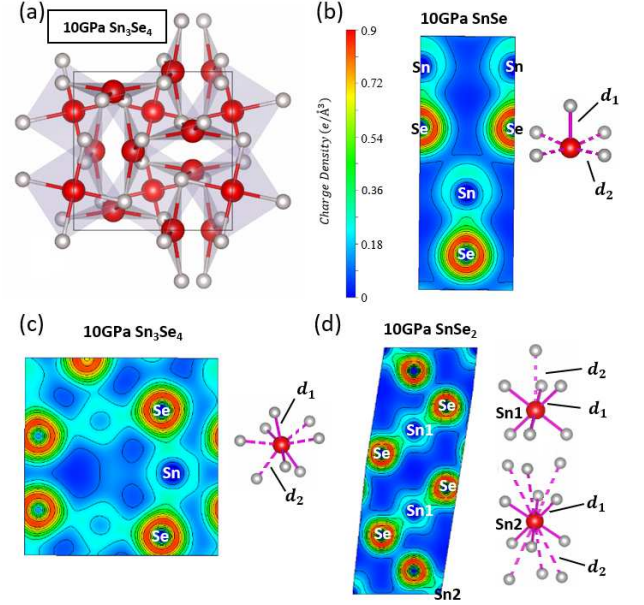


FIG. 5. (a) The conventional unit cell of  $\text{Sn}_3\text{Se}_4$ ; red and grey spheres represent the Sn and Se atoms, respectively. Charge density distributions in  $\text{SnSe}$  (b),  $\text{Sn}_3\text{Se}_4$  (c) and  $\text{SnSe}_2$  (d) at 10 GPa; the corresponding coordination polyhedra are also given.

structure calculations show that the new  $\text{Sn}_3\text{Se}_4$  compound exhibits a metallic behavior, in sharp contrast to existing Sn-Se semiconductors. It is predicted that the metallization of  $\text{Sn}_3\text{Se}_4$  leads to a superconducting transition at much lower pressures than what was previously expected for the Sn-Se binary system. Electron density and Bader charge analysis have been carried out to explore the mixed characters of the chemical bonding in  $\text{Sn}_3\text{Se}_4$ . This work suggests that new compounds with unexpected stoichiometries may exist in the IV-VI groups; novel and interesting properties may be sought within these unusual compounds.

We are grateful for the financial support from the Early Career Scheme of RGC under project No. 27202516 and the research computing facilities offered by ITS, HKU. The experimental work is supported by NSAF (Grant No: U1530402) and NSFC (Grant No: 21501162). HPCAT (Geophysical Lab) operations are supported by DOE-NNSA under Award No. DE-NA0001974 and DOE-BES under Award No. DE-FG02-99ER45775, with partial instrumentation funding by NSF. APS is supported by DOE-BES, under Contract No. DE-AC02-06CH11357.

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