Tin-selenium binary compounds are important semiconductors and widely applied in photovoltaic, thermoelectric, 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 (SnSe₂), 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 lamellar SnSe (B16-type structure in the Pnma space group) undergoes a pressure-induced structural phase transition to the B33 structure (Cmcmc space group) at about 10.5 GPa [6]. Under further compression, SnSe transforms into the B2 structure (Pm3m space group) and this phase was found to exhibit a superconducting transition at low temperatures above 58 GPa [7]. SnSe₂ is also a layered semiconductor with a hexagonal CdI₂-type crystal structure (P3m1 space group) [8]. From x-ray diffraction (XRD), it was found that SnSe₂, which is important for photovoltaic applications [9], shows a second polytype with a space group of R3m [10]. On the other hand, the compound Sn₂Se₃ has a controversial stoichiometry; it was argued that this compound is simply a superposition of SnSe and SnSe₂ [11].

Novel phases and compounds may be synthesized under high pressures [12,13]. Theory-assisted material discovery based on the 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, Ca₂C and Ca₃C₂, were predicted and successfully synthesized [18]. In the Zr-B binary system, Zr₃B₂ and Zr₃B₃ were predicted to be metastable below 50 GPa from the evolutionary approach [19]. Zhang et al. predicted some unexpected stable 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 µm 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 were 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 SnSe₂, that are energetically preferable at low pressures. As expected, SnSe goes through a phase transition from the Pnma structure through Cmcmc to a higher symmetry B2 structure with increasing pressure.
The high-pressure crystal structures and the corresponding phase transition pressures are in good agreement with experimental observations [6,7], indicating the reliability of our calculations. SnSe₂ has a CdI₂-type structure with a space group of P3̅m1 at 0 GPa, and it transforms into the R3̅m space group at 5 GPa. These two competing phases of SnSe₂ have very similar enthalpies at 0 GPa; e.g., R3̅m is only ~3.5 meV/atom higher in enthalpy than P3̅m1, which may explain the experimental observations of different SnSe₂ polytypes. It is also noted that the convex hull at 20 GPa does not contain the 1:2 stoichiometry, indicating that SnSe₂ becomes unstable and decomposes at high pressures. On the other hand, a new compound with an unexpected stoichiometry, 3:4, in the I4̅3d space group is predicted to be energetically stable at 10 GPa. It is likely that SnSe₂ spontaneously decomposes into Sn₃Se₄ and Se at high pressures. As can be seen from the convex hulls, Sn₃Se₄ is energetically preferable up to the highest pressure considered in this work. The large pressure range where Sn₃Se₄ is energetically preferable makes it possible to synthesize the compound. Unlike the layered crystal structures of SnSe and SnSe₂, Sn₃Se₄ has a more densely packed ThI₃P₄-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 ThI₃P₄-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 Sn₃Se₂ in the I4̅/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 dynamical stability of Sn₃Se₄ 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 Sn₃Se₄ 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 Sn₃Se₄ in the I4̅3d 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 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 Sn₃Se₄ phase can be clearly identified from the XRD patterns. The nonfitted 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 I4̅3d. These experimental results are in excellent agreement with our calculations; the theoretical lattice parameter is 8.3 Å at 16 GPa and 0 K. The Sn₃Se₄ 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...
Comparing to SnSe, Sn becomes a superconductor at temperatures below 4.5 K [7]. The conduction bands mainly contain the Se $4p$ states, showing significant hybridizations; the top of the valence bands are largely the Se $4s$ and $3p$ orbitals; above Fermi level, the main contribution comes from the Sn $5p$ orbitals. For the new Sn$_3$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, a majority of the electronic states originate from the Se $4p$ and Sn $5s$ orbitals. From the electronic structures of SnSe$_2$ [see Fig. 4(c)], it is interesting that a band gap opens up at Fermi level, suggesting that 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 valence 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, Sn$_3$Se$_4$ has a much lower 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 the Supplemental Material) [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 Sn$_3$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 Sn$_3$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. Because of the layered crystal structures of SnSe and 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 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

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**FIG. 3.** Le Bail fitting plot of in situ XRD patterns of Sn$_3$Se$_4$ under 16.4 GPa and 1225 K. The experimental and simulated data are 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.

**FIG. 4.** Projected electronic band structures along high symmetry paths (left) and projected DOS (right) of SnSe (a), Sn$_3$Se$_4$ (b), and SnSe$_2$ (c), at 10 GPa. Fermi level is located at 0 eV. Different circle sizes correspond to the projected weights of different orbitals.
SnSe and SnSe₂ atoms have a distribution in Sn that is significantly different from those in SnSe and SnSe₂. Because of the very similar Bader charges of the nonequivalent Sn or Se atoms in SnSe, 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 SnSe [47], Pb₁₋ₓSnₓSe [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 Sn₃Se₄ with an unusual stoichiometry is predicted to be stable above 10 GPa. Compared to the layered crystal structures of SnSe and SnSe₂, Sn₃Se₄ is more densely packed. Our calculations have been verified by the successful synthesis of Sn₃Se₄ 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. Electron density and Bader charge analysis have been carried out to explore the mixed characters of the chemical bonding in Sn₃Se₄. 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.

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TABLE I. Bader charge analysis on different Sn–Se compounds at 10 GPa. Because of the very similar Bader charges of the nonequivalent Sn or Se atoms in SnSe₂, only the average values are shown.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Sn (e)</th>
<th>Se (e)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SnSe</td>
<td>0.82</td>
<td>−0.82</td>
</tr>
<tr>
<td>Sn₁₃Se₄</td>
<td>0.94</td>
<td>−0.70</td>
</tr>
<tr>
<td>SnSe₂</td>
<td>1.15</td>
<td>−0.58</td>
</tr>
</tbody>
</table>

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[23] The projector-augmented wave method (PAW) [25] combined with the generalized gradient approximation (GGA) in the Perdew-Burke and Ernzerhof (PBE) form [26] was applied in all DFT calculations using VASP [27]. A cutoff energy of 350 eV was used for expanding the wave functions. Brillouin zone was sampled adopting the Γ-centered Monkhorst-Pack method with a density of about $2\pi \times 0.04 \text{ Å}^{-1}$. The convergence criterion for electronic self-consistent calculation was $10^{-6}$ eV.


[27] The variable-composition evolutionary search was performed using USPEX [29]. New crystal structures were generated using the following schemes: heredity (40%), random (20%), softmutation/coormutation (20%), and transmutation (20%).


[36] Phonon dispersions were computed using the small displacement method implemented in Phonopy [38]. A $2 \times 2 \times 2$ supercell containing 112 atoms was used. For accurate atomic forces, the convergence criterion for electronic self-consistent calculations was increased to $10^{-8}$ eV.


