Two pressure-induced superconducting transitions in SnBi₂Se₄ explored by data-driven materials search: new approach to developing novel functional materials including thermoelectric and superconducting materials

Ryo Matsumoto¹,4, Zhufeng Hou², Hiroshi Hara¹,4, Shintaro Adachi¹, Hiroyuki Takeya¹, Tetsuo Irifune⁵, Kiyoyuki Terakura³, and Yoshihiko Takano¹,4

¹International Center for Materials Nanoarchitectonics (MANA), National Institute for Materials Science, Tsukuba, Ibaraki 305-0047, Japan
²Research and Services Division of Materials Data and Integrated System (MaDIS), National Institute for Materials Science, Tsukuba, Ibaraki 305-0047, Japan
³Center for Materials Research by Information Integration (CMII), National Institute for Materials Science, Tsukuba, Ibaraki 305-0047, Japan
⁴University of Tsukuba, Tsukuba, Ibaraki 305-8577, Japan
⁵Geodynamics Research Center, Ehime University, Matsuyama 790-8577, Japan

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Candidates for new thermoelectric and superconducting materials, which have narrow band gaps and flat bands near band edges, were searched by high-throughput first-principles calculation from an inorganic materials database. The synthesized SnBi₂Se₄ among the target compounds showed a narrow band gap of ~200 meV and a thermal conductivity of ~1 W K⁻¹ m⁻¹ at ambient pressure. The sample SnBi₂Se₄ showed a metal–insulator transition at 11.1 GPa, as predicted by theoretical estimation. Furthermore, two pressure-induced superconducting transitions were discovered under 20.2 and 47.3 GPa. The data-driven search is a promising approach to discovering new functional materials.

Data-driven materials sciences (materials informatics,¹ materials genome initiative,²² chemometrics,³¹ and so on) have recently brought remarkable results.¹⁻¹⁰ For example, the discovery of new cathode materials to extend the lifetime of lithium ion batteries can be accelerated by using a high-throughput screening approach.¹¹ On the other hand, the search for new functional thermoelectric materials and/or superconductors is still mostly conducted through carpet-bombing-type experiments depending on the experience and inspiration of the researcher.

In this study, we exhaustively searched for new candidate thermoelectric and superconducting materials by first-principles calculation using a guideline that is characterized by specific band structures of “flat band” near the Fermi level, such as multivalley,¹² pudding mold,¹³ and topological¹⁴ structures. If such kinds of flat band approach the Fermi level, the thermoelectric properties of electrical conductivity and Seebeck coefficient would be enhanced.¹³,¹⁵ If the flat band crosses the Fermi level, superconductivity would be realized owing to the high density of states (DOS).¹⁶⁻¹⁸

Single-crystal samples of the compound chosen by the above-mentioned screening were successfully synthesized. The transport properties of the obtained samples were evaluated under ambient and high pressures. Here, we report the discoveries of not only the pressure-induced metal–insulator transition of the sample but also superconducting phases under additional pressure. In this work, we successfully demonstrate the exploration of new functional materials by data-driven search.

To search for new thermoelectric and superconducting materials, we conducted high-throughput first-principles calculations on about 1570 candidates of ternary compounds listed in the inorganic materials database AtomWork.¹⁹ The selection of these candidate compounds was guided by the following restrictions: abundant and nontoxic or less toxic constituent elements and number of atoms of less than 16 per primitive unit cell. The first-principles calculations were carried out using the projector-augmented wave (PAW) method²⁰ within the generalized gradient approximation (GGA), in which the Perdew–Burke–Ernzerhof (PBE)²¹ exchange–correlation functional was used. For every candidate compound, we first carried out four steps of first-principles calculations including structure relaxation, self-consistent field (SCF) calculations, band structure, and DOS of its crystal structure. From the calculated band structures and DOSs, we narrowed down the number of candidates by selecting the compounds that shall have a real or pseudo energy gap. Additionally, a certain size (e.g., ≤0.6 eV in the GGA-PBE calculations) in the band gap, high DOSs near the Fermi level or the valence and conduction band edges, and the flat band were considered in the selection criteria. Here, a phonon state was not considered as a screening component of a current stage to include nonphonon-mediated superconductors. By this screening, the number of candidate compounds was reduced to 45. Then, we carried out the aforementioned four steps of first-principles calculations for these 45 compounds under high pressure of 10 GPa. By checking whether the band gap is decreased (or even the metallic behavior appears), we screened out 27 promising compounds for our further studies to uncover their functionalities. Through the above screening procedures, SnBi₂Se₄ was chosen as a new candidate thermoelectric and superconducting material. The details of our screening scheme in the high-throughput first-principles calculations and the complete results will be given elsewhere.

Figure 1 shows (a) the crystal structure of SnBi₂Se₄ (trigonal R₃m structure, lattice constants of a = b = 4.188 Å and c = 39.46 Å²²), drawn using VESTA,²³ (b) the band structure, and (c) the total DOS of SnBi₂Se₄ determined by GGA-PBE calculations with spin–orbital coupling. We can see that SnBi₂Se₄ has a narrow band gap of ~200 meV and that both the top valence band along several k-point paths and the bottom conduction band along Γ–Z are quite flat. The valence bands especially show a high total DOS near the Fermi level. The top valence band is contributed mainly by the Se 4p and Sn 5s states, while the bottom conduction band...
is contributed mainly by the Bi 6s state. Such a band structure satisfies the screening condition. The band structures under high pressures suggest that the band edges approach the Fermi level at around 5–10 GPa, indicating a pressure-induced metal–insulator transition.

Single crystals of SnBi$_2$Se$_4$ were grown by a melt and slow-cooling method. Starting materials of Bi grains (99.9%), Sn grains (99.99%), and Se chips (99.999%) were put into an evacuated quartz tube in the stoichiometric composition of SnBi$_2$Se$_4$. The ampoule was heated at 300 °C for 8 h and subsequently at 550 °C for 10 h. The obtained powders were ground and loaded into an evacuated quartz tube. The sample was heated again at 700 °C for 10 h and slowly cooled to 620 °C for 8 h followed by furnace cooling.

The crystal structure of the obtained sample was investigated by powder X-ray diffraction (XRD) using Mini Flex 600 (Rigaku). The chemical composition of the sample was evaluated by single-crystal structural analysis using XtaLAB mini (Rigaku) and energy-dispersive X-ray spectrometry (EDX) analysis using JSM-6010LA (JEOL). Figure 2 shows the powder XRD pattern of the pulverized sample. Most of the observed peaks were well indexed to a trigonal R$\bar{3}m$ structure with lattice constants of $a = b = 4.26$ Å and $c = 39.17$ Å, except for a few weak peaks of impurity phases. The single crystal structural analysis revealed that the actual composition is SnBi$_{1.72}$Se$_{3.54}$ calculated from the site occupancies. The EDX analysis showed the composition of SnBi$_{1.64}$Se$_{3.53}$, which is in accordance with the single crystal structural analysis.

The thermoelectric properties of the obtained SnBi$_2$Se$_4$ were investigated. Figure 3 shows the temperature dependences of (a) electrical resistivity, (b) Seebeck coefficient, (c) carrier concentration, and (d) thermal conductivity under ambient pressure, measured using a physical property measurement system (Quantum Design PPMS) with thermal transport option. In accordance with the slope of the Arrhenius plot for resistivity, the sample was determined to have a narrow band gap of 354 meV near room temperature, which is consistent with the GGA-PBE calculations. The negative Seebeck coefficient and negative slope of the Hall voltage indicate the n-type nature of the sample, which may be caused by vacancy defects. The thermal conductivity of $\sim 1$ W·K$^{-1}$·m$^{-1}$ was considerably low even near room temperature. On the other hand, the small power factor of 9.1 $\mu$W·m$^{-1}$·K$^{-2}$ and the figure of merit (ZT) of 0.0038 near room temperature were observed as shown in Figs. 3(e) and 3(f), caused by a high resistivity. It is possible to improve these thermoelectric properties by decreasing resistivity using carrier doping$^{24}$ or high-pressure application.$^{25-27}$ The calculations of power factor based on the band structures under ambient and high pressures using a BoltzTrap code$^{28}$ suggest that the power factor could be enhanced by applying pressure around the metal–insulator transition, owing to a decrease in resistivity. As a further study, it is necessary to develop innovative techniques of measuring thermoelectric properties under high pressures. We therefore focused on the resistivity of SnBi$_2$Se$_4$ under high pressures.

To explore the pressure-induced metal–insulator transition and superconductivity in SnBi$_2$Se$_4$, we performed electrical resistivity measurements under high pressures using an originally designed diamond anvil cell with boron-doped diamond electrodes.$^{29-32}$ The SnBi$_2$Se$_4$ single crystal was placed at the center of the bottom anvil where the boron-doped diamond electrodes were fabricated. Except for the sample space and electrical terminal, the surface of the bottom anvil was covered by an undoped diamond insulating layer. Details of the cell configuration are described in the literature.$^{31,32}$ The cubic boron nitride powders with a ruby manometer were used as a pressure-transmitting medium.
The applied pressures were estimated on the basis of the fluorescence from ruby powders\(^{33}\) and the Raman spectrum from the culet of a top diamond anvil\(^{34}\) using an inVia Raman microscope (RENISHAW). The pressure at low temperatures slightly increases in this diamond anvil cell.

Figure 4(a) shows the temperature dependence of resistance for SnBi\(_2\)Se\(_4\) under various pressures from 1.9 to 16.9 GPa. The band gaps estimated from the Arrhenius plot near room temperature were labeled at each pressure. The resistance and band gap decreased with increasing applied pressure. The metallic conductivity of the sample appeared at 11.1 GPa, indicating a pressure-induced metal–insulator transition. This behavior is qualitatively consistent with the theoretical calculation. The high thermoelectric performance of this compound would be expected at a pressure around the metal–insulator transition, since the flat bands with high DOSs approach the Fermi level.

Figure 4(b) shows the temperature dependence of resistance from 20.2 to 42.9 GPa. A pressure-induced superconductivity with clear zero resistance was observed above 20.2 GPa. The maximum onset transition temperature (\(T_{\text{onset}}\)) and zero-resistance temperature (\(T_{\text{zero}}\)) were 2.5 and 2.1 K under 42.9 GPa, respectively. The critical current \(I_c\) and upper critical field \(H_{\text{ab}}^c(0)\) were 35 \(\mu\)A and 2.1 T under 42.9 GPa, respectively, as shown in Fig. 5. \(H_{\text{ab}}^c(0)\) was estimated from the Werthamer–Helfand–Hohenberg (WHH) approximation\(^\text{35}\) for the Type II superconductor in a dirty limit. The \(T_c\), \(I_c\), and \(H_{\text{ab}}^c(0)\) values in this superconducting phase were almost independent of pressure.
Pressure phase diagram of SnBi$_2$Se$_4$. 

Surprisingly, the $T_c$ of SnBi$_2$Se$_4$ increased with the application of additional pressure, which implies the discovery of a second superconducting phase. The temperature dependence of resistance from 42.9 to 71.6 GPa is summarized in Fig. 4(c). $T_c$ was suddenly enhanced from 2.5 K under 42.9 GPa to 5.9 K under 63.2 GPa. In the higher $T_c$ phase, the maximum $I_c$ and $H_{c2}(0)$ were enhanced up to 525 µA and 3.2 T, respectively, under 63.2 GPa, compared with those in the lower $T_c$ phase.

Figure 6 shows a pressure phase diagram of SnBi$_2$Se$_4$ single crystal. The resistance of the sample was markedly decreased by applying pressure, and the metal–insulator transition occurred at 11.1 GPa. In this region, high thermoelectric properties can be expected in this sample.

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