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Low Lattice Thermal Conductivity in Pb$_2$Bi$_6$Se$_{14}$, Pb$_3$Bi$_2$S$_6$, and PbBi$_2$S$_4$: Promising Thermoelectric Materials in the Cannizzarite, Lillianite, and Galenobismuthite Homologous Series

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Abstract

The thermoelectric properties of Pb₅Bi₆Se₁₄, a member of the cannizzarite homologous series; Pb₃Bi₂S₆, a member of the lillianite homologous series; and PbBi₂S₄, a member of the galenobismuthite series were investigated over the temperature range of 300 K to 723 K. The samples were synthesized by a solid state reaction of the binary precursors PbQ and Bi₂Q₃ (Q = S, Se) in evacuated and sealed quartz tubes, followed by pulsed electric current sintering. The crystal structure of Pb₅Bi₆Se₁₄ consists of alternating two-dimensional infinite layers of PbSe and Bi₂Se₃. In the Pb₅Bi₆Se₁₄ sintered compacts, the \( ab \)-plane was preferentially oriented perpendicular to the pressing direction, resulting in highly anisotropic electrical and thermal transport properties. The crystal structure of Pb₃Bi₂S₆ is formed by stacking NaCl-type (Pb/Bi)S layers with a mirror as twinning operation, while that of PbBi₂S₄ consists of the NaCl-type and Bi₂S₃-type strips (broken layers) of finite widths. The crystal grains of Pb₃Bi₂S₆ and PbBi₂S₄ were grown randomly, leading to nearly isotropic electrical and thermal transport properties in the sintered compacts. For all samples, an \( n \)-type degenerate semiconductor-like behavior was found, providing a notable thermoelectric power factor of \(~3.0 \, \mu W \, K^{-2} \, cm^{-1}\) at 705 K for Pb₅Bi₆Se₁₄, \(~2.4 \, \mu W \, K^{-2} \, cm^{-1}\) at 715 K for Pb₃Bi₂S₆, and \(~2.6 \, \mu W \, K^{-2} \, cm^{-1}\) at 515 K for PbBi₂S₄ in direction perpendicular to the pressing direction. Moreover, these materials exhibited effective phonon scattering, presumably at the interfaces between layers, leading to extremely low lattice thermal conductivity in the range of \(0.29 \, W \, K^{-1} \, m^{-1}\) to \(0.80 \, W \, K^{-1} \, m^{-1}\) over the temperature range of 300 K to 723 K. The highest \( ZT \) of \(~0.46\) at 705 K was observed in Pb₅Bi₆Se₁₄ for the \( ab \)-plane direction.
1. Introduction

An enormous amount of waste heat generated from various sources could be converted to useful electrical energy to improve energy management and sustainability. Because the heat can be directly converted to electrical energy using thermoelectric generators, it promises waste heat recovery in vehicle exhaust, industrial processes, fuel combustion, and so on. A thermoelectric generator is a solid state device that consists mainly of $p$- and $n$-type semiconductors (thermoelectric materials) and its performance depends on the thermoelectric figure of merit ($ZT$). The efficiency of a thermoelectric material increases with increasing $ZT$, defined as $ZT = \sigma S^2 T / \kappa_{\text{total}}$, where $\sigma$ is the electrical conductivity, $S$ is the Seebeck coefficient, $T$ is the temperature, and $\kappa_{\text{total}}$ is the total thermal conductivity. The quantity $\sigma S^2$, which is known as the thermoelectric power factor, is the key to achieving high electrical performance and can be optimized by tuning the carrier concentration of materials. The $\kappa_{\text{total}}$ is a combined property by two parts, $\kappa_{\text{total}} = \kappa_{\text{el}} + \kappa_{\text{lat}}$: the electronic thermal conductivity ($\kappa_{\text{el}}$) and lattice thermal conductivity ($\kappa_{\text{lat}}$). The former is directly related to the electrical conductivity through the Wiedemann–Franz relation: $\kappa_{\text{el}} = LT \sigma$, where $L$ is the Lorenz number. Thus, one strategy to reduce the $\kappa_{\text{total}}$ is to minimize $\kappa_{\text{lat}}$ which is a carrier-independent parameter.

The most widely used thermoelectric materials are Bi$_2$Te$_3$–Sb$_2$Te$_3$ for near-room-temperature applications and PbTe for intermediate-temperature ($\sim$700 K) applications. The $ZT$ of PbTe-based materials had been limited to about unity until 2000 but has been dramatically enhanced over 2.0 by nanostructuring. The nanostructuring results in a significant reduction in $\kappa_{\text{lat}}$, allowing an enhancement in the $ZT$. Recently, efforts have been devoted to develop high-$ZT$ thermoelectric materials using nanolayered structure approaches (for example, cobalt oxides, titanium disulfide, and tin selenide).

The homologous series of layered compounds are great places to look for new classes of thermoelectric materials. A structure of the homologous series is built on the same structural principle with certain module(s) expanding in various dimension(s) by regular increments. Therefore, in such homologous compounds, the thermoelectric properties can be tuned by modifying the structural module(s). In the past decade, several homologous layered structures have been reported, including $A_m[M_1'_{1+n}Se_{2+2}]_{2m}[M_2'_{2+l+n}Se_{2+3+l+n}]$ ($A =$ alkali,
alkali earth element; M', M'' = main group element)\textsuperscript{37–38}, Cs\textsubscript{4}[Bi\textsubscript{2}Te\textsubscript{3}]\textsubscript{m}\textsuperscript{28,39–41}, CsM\textsubscript{m}Bi\textsubscript{2}Te\textsubscript{5}\textsuperscript{42,43}, and tetradymite homologous series [MTe\textsubscript{n}][Bi\textsubscript{2}Te\textsubscript{3}]\textsubscript{m} (M = Ge, Sn, Pb)\textsuperscript{44–52}. A record high ZT below room temperature was found in CsBi\textsubscript{4}Te\textsubscript{6} with ~0.8 at 225 K.\textsuperscript{39} In this study, we assessed for the first time the high-temperature thermoelectric properties of Pb\textsubscript{5}Bi\textsubscript{6}Se\textsubscript{14}, a member of the cannizzarite homologous series; Pb\textsubscript{5}Bi\textsubscript{2}S\textsubscript{6}, a member of the lillianite homologous series; and PbBi\textsubscript{2}S\textsubscript{4}, a member of the galenobismuthite series.

Pb\textsubscript{5}Bi\textsubscript{6}Se\textsubscript{14} originates from the mineral cannizzarite (Pb\textsubscript{46}Bi\textsubscript{54}S\textsubscript{127})\textsuperscript{23–26,53} and is a member (n = 1, m = 1) of the cannizzarite homologous series with a general formula [(PbSe)\textsubscript{5}][(Bi\textsubscript{2}Se\textsubscript{3})\textsubscript{3}]\textsubscript{m}, in which two different module layers PbSe and Bi\textsubscript{2}Se\textsubscript{3} are Pb/Bi mixed occupied. As shown in Figure 1(a), the crystal structure of Pb\textsubscript{5}Bi\textsubscript{6}Se\textsubscript{14} consists of alternating infinite PbSe- and Bi\textsubscript{2}Se\textsubscript{3}-type layers.\textsuperscript{54} The two layers are stacked alternately along c-axis to build a three-dimensional structure and vary their thickness to form different members in the homology. This natural planar superlattice structural feature prompted us to investigate the thermoelectric properties of Pb\textsubscript{5}Bi\textsubscript{6}Se\textsubscript{14}. Recently, Shelimova et al.\textsuperscript{55,56} measured the thermoelectric properties of three members of cannizzarite homologous series Pb\textsubscript{5}Bi\textsubscript{6}Se\textsubscript{14}, Pb\textsubscript{5}Bi\textsubscript{12}Se\textsubscript{23}, and Pb\textsubscript{5}Bi\textsubscript{18}Se\textsubscript{32} over the temperature range of 80 K to 370 K. The melt-grown ingots of all systems showed low value of \(\kappa_{\text{lat}}\); for example room-temperature \(\kappa_{\text{lat}}\) of Pb\textsubscript{5}Bi\textsubscript{6}Se\textsubscript{14} was 0.72 W K\textsuperscript{−1} m\textsuperscript{−1}. Interestingly, it was recently found that Ag doping of Pb\textsubscript{5}Bi\textsubscript{12}Se\textsubscript{23} results in superconductivity.\textsuperscript{57} In order to evaluate their potential for thermoelectric applications, the high-temperature thermoelectric properties of the cannizzarite homologous series should be investigated on highly oriented samples. These investigations provide insights for achieving high ZT in the cannizzarite homologous series.

Pb\textsubscript{3}Bi\textsubscript{2}S\textsubscript{6} is a member of the lillianite homologous series, of which the crystal structure is formed by stacking NaCl-type (Pb/Bi)S layers with a mirror as twinning operation,\textsuperscript{23,26,58–61} as shown in Figure 1(b). The members of the lillianite series evolve by the thickness of the (Pb/Bi)S layers. PbBi\textsubscript{2}S\textsubscript{4} belongs to the galenobismuthite homologous series with an isostructural crystal structure to CaFe\textsubscript{2}O\textsubscript{4}.\textsuperscript{23,26,62–64} In the crystal structure, the NaCl- and Bi\textsubscript{2}S\textsubscript{3}-type layers are broken into strips of finite widths (Figure 1(c)). Like the cannizzarite homologous series, the complex crystal structures of the lillianite and galenobismuthite homologous series are expected to yield the low lattice thermal conductivity and two lillianite members
KxSn6−2xBi2+2xSe9 and KSn5Bi2Se13 were measured only for the near-room-temperature $\sigma$ and $S$.

In this paper, we report the high-temperature thermoelectric properties of the cannizzarite homologous member Pb$_5$Bi$_6$Se$_{14}$, the lillianite homologous member Pb$_3$Bi$_2$S$_6$, and the galenobismuthite member PbBi$_2$S$_4$. The $\sigma$, $S$, and $\kappa_{\text{total}}$ of their sintered compacts were measured perpendicular (in-plane) and parallel (out-of-plane) to the pressing direction over the temperature range of 300 K to 723 K. While anisotropic electrical and thermal transport properties were found in Pb$_5$Bi$_6$Se$_{14}$, nearly isotropic electrical and thermal transport properties were found in Pb$_3$Bi$_2$S$_6$ and PbBi$_2$S$_4$. We demonstrate a notable power factor, $\sigma S^2$ and an extremely low $\kappa_{\text{lat}}$ in Pb$_5$Bi$_6$Se$_{14}$, Pb$_3$Bi$_2$S$_6$, and PbBi$_2$S$_4$. The strategy for achieving high $ZT$ in these homologous series is discussed.

2. Experimental Section

2.1. Synthesis

Elemental lead (Pb; 99.9999%, Osaka Asahi Metal MFG), elemental bismuth (Bi; 99.9999%, Osaka Asahi Metal MFG), elemental selenium (Se; 99.999%, Kojundo Chemical Laboratory), and elemental sulfur (S; 99.9999%, Kojundo Chemical Laboratory) were used as starting materials without further purification. Binary chalcogenides PbSe, PbS, Bi$_2$Se$_3$, and Bi$_2$S$_3$ were prepared first. Ternary chalcogenides Pb$_5$Bi$_6$Se$_{14}$, Pb$_3$Bi$_2$S$_6$, and PbBi$_2$S$_4$ were then prepared by a solid state reaction from the binary chalcogenides.

2.1.1. Pb$_5$Bi$_6$Se$_{14}$

In the preparation of binary precursor PbSe, a stoichiometric mixture of elements with a total mass of ~10 g was loaded into a fused silica tube of 12 mm outer diameter × 10 mm inner diameter. The tube was evacuated to a pressure of ~10$^{-3}$ Pa and then flame-sealed. The mixture was heated to 773 K at a rate of ~40 K h$^{-1}$, heated to 1393 K at a rate of ~80 K h$^{-1}$, and then held at 1393 K for 12 h. The sample was then cooled to room temperature over 2 h.
In the preparation of Bi$_2$Se$_3$ starting material, a stoichiometric amount of Bi and Se with a total mass of ~10 g was loaded into a fused silica tube of 12 mm outer diameter $\times$ 10 mm inner diameter. The tube was evacuated to a pressure of $\sim$10$^{-3}$ Pa and then flame-sealed. The mixture was heated to 773 K at a rate of $\sim$40 K h$^{-1}$, heated to 1173 K at a rate of $\sim$60 K h$^{-1}$, and then held at 1173 K for 12 h. The sample was then cooled to room temperature over 2 h.

For the preparation of Pb$_5$Bi$_6$Se$_{14}$, the melt grown ingots of PbSe and Bi$_2$Se$_3$ were hand-ground. A stoichiometric amount of PbSe (4.214 g) and Bi$_2$Se$_3$ (5.786 g) powders with a total mass of 10 g was well mixed and loaded into a fused silica tube of 12 mm outer diameter $\times$ 10 mm inner diameter. The tube was evacuated to a pressure of $\sim$10$^{-3}$ Pa and then flame-sealed. The mixture was heated to 873 K at a rate of $\sim$290 K h$^{-1}$, held at 873 K for 120 h, and then slowly cooled to room temperature at a rate of $\sim$20 K h$^{-1}$. To improve homogeneity of the product, the powder obtained was thoroughly mixed and heating repeatedly under the same condition at 873 K for 120 h. The total reaction time was 240 h.

### 2.1.2. Pb$_3$Bi$_2$S$_6$ and PbBi$_2$S$_4$

A pre-process for the binary precursors PbS and Bi$_2$S$_3$ are same as above. The stoichiometric mixture of Pb and S was loaded into a carbon-coated fused silica tubes. The tubes were evacuated to a pressure of $\sim$10$^{-3}$ Pa and then flame-sealed. The reaction mixture was heated to 773 K at a rate of $\sim$40 K h$^{-1}$, heated to 1423 K at a rate of $\sim$80 K h$^{-1}$, and then held at 1423 K for 12 h before cooling to room temperature over 2 h. The stoichiometric mixture of Bi and S loaded into a sealed fused silica tube was heated to 773 K at a rate of $\sim$40 K h$^{-1}$, heated to 1223 K at a rate of $\sim$60 K h$^{-1}$, and then held at 1223 K for 12 h before cooling to room temperature over 2 h.

For the preparation of Pb$_3$Bi$_2$S$_6$, the melt grown ingots of binary chalcogenides PbS and Bi$_2$S$_3$ were hand-ground. A stoichiometric ratio of PbS (5.826 g) and Bi$_2$S$_3$ (4.174 g) with a total mass of 10 g was well mixed and then loaded into a fused silica tube of 12 mm outer diameter $\times$ 10 mm inner diameter. The tube was evacuated to a pressure of $\sim$10$^{-3}$ Pa and then flame-sealed. The mixture was heated to 973 K at a rate of $\sim$340
K h\(^{-1}\), held at 973 K for 120 h, and then slowly cooled to room temperature at a rate of \(\sim 30\) K h\(^{-1}\). Annealing was repeated at the same temperature after grinding/mixing powder obtained to improve homogeneity of the product. The total reaction time was 240 h.

A same procedure was applied for the preparation of PbBi\(_2\)S\(_4\) with a stoichiometric amount of hand-ground PbS (3.176 g) and Bi\(_2\)S\(_3\) (6.824 g) with a total mass of 10 g. The mixture was heated to 973 K at a rate of \(\sim 340\) K h\(^{-1}\), held at 973 K for 120 h, and then slowly cooled to room temperature at a rate of \(\sim 30\) K h\(^{-1}\) in a vacuum-sealed silica tube. This annealing step was repeated to improve homogeneity of the powder obtained. The total reaction time was 240 h.

### 2.2. Sintering

The samples were sintered under a uniaxial pressure to obtain the dense compacts. The powders of ternary chalcogenides Pb\(_5\)Bi\(_6\)Se\(_{14}\), Pb\(_3\)Bi\(_2\)S\(_6\), and PbBi\(_2\)S\(_4\) prepared above were re-ground to pass through a 20 µm size sieve and then placed into graphite dies. In each material, the graphite die was inserted into the pulsed electric current sintering apparatus (SPS-515S, Fuji Electronic Industrial). For selenide samples, sintering was performed at 823 K for 2 h under a uniaxial pressure of 30 MPa in vacuum \((7.0 \times 10^{-3}\) Pa). For sulfide samples, sintering was performed at 773 K for 2 h under a uniaxial pressure of 30 MPa in vacuum \((7.0 \times 10^{-3}\) Pa). In all cases, the heating and cooling rates were 10 K min\(^{-1}\) and 20 K min\(^{-1}\), respectively. In order to improve the homogeneity and prepare the oriented sintered compacts, a 2 h long sintering time was applied.

The mass density of the sintered compacts was determined using the Archimedes method. The sintered density of all samples was found to be greater than 99\% of the theoretical density (Table S1 in the Supplementary Information).

For each material, we prepared three sintered samples with different sizes for electrical and thermal transport measurements in the direction of perpendicular (in-plane) and parallel (out-of-plane) to the pressing direction. The cylindrical samples of \(\sim 10\) mm diameter \(\times \sim 11\) mm length were cut into bars and coins for out-of-plane electrical transport measurements and in-plane thermal transport measurements, respectively. The
disks of ~15 mm diameter × ~2 mm thickness were cut into bars for in-plane electrical transport measurements. The disks of ~10 mm diameter × ~2 mm thickness were used for out-of-plane thermal transport measurements.

2.3. Powder X-ray Diffraction and Scanning Electron Microscopy

The crystal structure of the synthetic powders and sintered compacts was examined by X-ray diffractionmetry (XRD; Rint-Ultima+, Rigaku) using the Cu Kα radiations over the 2θ range of 10°–80°. Both in-plane and out-of-plane XRD patterns of the sintered compacts were investigated in order to examine the crystal orientation. The microstructure of the sintered compacts was observed on the fractured sections parallel to the pressure direction by scanning electron microscopy (SEM; JSM-6610LV, JEOL, 20kV).

2.4. Electrical Transport Measurements

The Seebeck coefficient and electrical resistivity were measured simultaneously under He atmosphere using a temperature differential method and four-probe method, respectively (ZEM-3, ULVAC-RIKO) over the temperature range of 300 K to 723 K. The typical dimensions of the bars used for the in-plane measurements were ~3 mm × ~2 mm × ~12 mm and for out-of-plane measurements were ~3 mm × ~3 mm × ~11 mm. Seebeck coefficient and electrical resistivity were reproducible over heating and cooling cycles for all samples.

The Hall coefficient ($R_{\text{H}}$) of the sintered compacts was measured at room temperature with a home-built system under a magnetic field of 0 T to 2.3 T. The typical sample dimensions were ~5 mm × ~5 mm × ~0.3 mm. The Cu contact wires were attached to the samples using In-rich In-Ga paste. The room-temperature Hall coefficient is given in Table S2 in the Supplementary Information.

2.5. Thermal Transport Measurements
The total thermal conductivity ($\kappa_{\text{total}}$) was calculated from the thermal diffusivity ($D$), heat capacity ($C_P$), and sintered mass density ($d$) using the expression $\kappa_{\text{total}} = DC_Pd$. The thermal diffusivity was directly measured and the heat capacity was indirectly derived using a standard sample (Pyroceram 9606, Netzsch) using the laser flash method (LFA 457 MicroFlash, Netzsch) under the Ar gas flow atmosphere (100 ml min$^{-1}$) over the temperature range 300 K to 723 K. The samples for in-plane measurements were square plates of ~10 mm × ~10 mm × ~2 mm and the samples for out-of-plane measurements were coins of ~ 10 mm in diameter and ~2 mm in thickness. Graphite spray coating was applied on the sample surface. The thermal diffusivity was reproduced over heating and cooling cycles for all sintered compacts. The thermal diffusivity and heat capacity are provided in Figures S1 and S2 in the Supplementary Information.

The heat capacity was confirmed by measuring the samples in differential scanning calorimetry (DSC; DSC 3500 Sirius, Netzsch) under an N$_2$ gas flow atmosphere (100 ml min$^{-1}$) over the temperature range 300 K to 473 K. The typical sample dimensions were ~5 mm × ~5 mm × ~1 mm. In the temperature range 300 K to 473 K, the discrepancy between the values of heat capacity measured in laser flash method and this DSC method is within the measurement error range of ~10% (Figure S2 in the Supplementary Information). The values obtained through laser flash method were used for determining the thermal conductivity over 300 K–723 K.

The sound velocities for longitudinal and transverse modes were measured at room temperature by the pulse-echo method with ultrasonic pulser/receivers (5077PR, Olympus), 5 MHz and 15 MHz longitudinal contact transducers, 5 MHz transverse contact transducers, and digitizing oscilloscope (WaveJet300A, Teledyne LeCroy). The typical dimensions of the square plates used for the in-plane measurements were ~10 mm × ~10 mm × ~2 mm and of the coins used for out-of-plane measurements were ~10 mm in diameter and ~2 mm in thickness.

3. Results and Discussion

3.1. Synthesis and Sintering
The powder X-ray diffraction (XRD) patterns of the samples before and after sintering are shown in Figure 2. In all cases, the synthetic and sintering processes used in this study produced single phases of the monoclinic Pb₅Bi₆Se₁₄ (P2₁/m)⁵⁴ (Figure 2(a)), orthorhombic Pb₃Bi₂S₆ (Cmcm)⁶¹ (Figure 2(b)), and orthorhombic PbBi₂S₄ (Pnma)⁶⁴ (Figure 2(c)). No secondary phase was observed. Table 1 lists the lattice parameters calculated from the measured powder XRD patterns of Pb₅Bi₆Se₁₄, Pb₃Bi₂S₆, and PbBi₂S₄ before and after sintering and known space groups⁵⁴,⁶¹,⁶⁴. The XTray diffractometer was calibrated with an external standard of Si. No significant changes of lattice parameters was found after sintering; for example lattice parameters of Pb₅Bi₆Se₁₄ are a = 2.1537 nm, b = 0.4202 nm, c = 1.6028 nm, β = 97.34° before sintering and a = 2.1540 nm, b = 0.4206 nm, c = 1.6047 nm, β = 97.39° after sintering.

Figure 2 also shows the out-of-plane XRD patterns for all sintered compacts. For the case of Pb₅Bi₆Se₁₄, a strong enhancement of the basal (00l) reflections was observed, showing that the crystalline c-axis is preferentially oriented along the pressing (out-of-plane) direction. The degree of (00l) orientation, referred to as the Lotgering factor f was calculated from the relation \( f = \left[ (P−P₀)/(1−P₀) \right] \) where \( P = \sum I(00l)/\sum I(hkl) \), where \( \sum I(00l) \) and \( \sum I(hkl) \) are the sums of the intensities of (00l) and (hkl) reflections, respectively, and \( P₀ \) is the value of \( P \) for a randomized powder sample.⁶⁷ While a perfectly orientated sample provides \( f = 1 \), a randomly orientated one provides \( f = 0 \). In this study, the Bragg reflections in the range 10° to 60° were used for calculation of \( f \). The \( f \) of out-of-plane XRD pattern of Pb₅Bi₆Se₁₄ is ~0.5. On the other hand, the powder and out-of-plane XRD patterns of the sulfide systems (Pb₃Bi₂S₆ and PbBi₂S₄) are very similar, indicating that these sintered compacts have a low degree of preferred orientation. These conclusions are supported by the results of the scanning electron microscopy (SEM) examinations of the sintered compacts, which is discussed below.

Figure 3 shows SEM micrographs of the fractured section of the sintered compacts (~15 mm diameter × ~2 mm thickness) that were fractured parallel to the pressure direction. The SEM micrographs of three sintered compacts of different sizes in each system are shown in Figure S3–S5. The examination of all the samples by SEM reveals a dense structure, which is consistent with the results of the Archimedes density measurements (Table S1 in the Supplementary Information). In the case of Pb₅Bi₆Se₁₄, a well-organized
texture was observed, and the preferential crystal orientation is apparent in the fractured section (Figure 3(a)). The crystal grains were preferentially grown in the direction perpendicular to the pressure applied during sintering, forming the needle-like grains with mean length of ~30 µm. This natural layering of the grains is probably due to the strong intralayer and weak interlayer bonding. In the case of sulfide systems, random textures were observed in Figure 3(b) and (c), meaning that the grains were grown randomly. The mean size of the plate-like grains of both samples is ~10 µm. Based on the orientation of texture observed, Pb$_5$Bi$_6$Se$_{14}$ is expected to provide anisotropic electrical and thermal transport properties, while the random texture of Pb$_3$Bi$_2$S$_6$ and PbBi$_2$S$_4$ provides nearly isotropic transport properties.

Since the sintered compacts prepared in this study consist of a single phase of Pb$_5$Bi$_6$Se$_{14}$, Pb$_3$Bi$_2$S$_6$, and PbBi$_2$S$_4$ and have a high sintered density (>99%), they are suitable for investigation of their thermoelectric properties.

### 3.2 Thermoelectric Properties of Pb$_5$Bi$_6$Se$_{14}$

The temperature dependences of the electrical conductivity ($\sigma$) and Seebeck coefficient ($S$) for the sintered compacts of Pb$_5$Bi$_6$Se$_{14}$ are shown in Figure 4(a) and (b), respectively. The data are consistent with an $n$-type degenerate semiconductor, namely, the $\sigma$ decreases while $S$ increases as the temperature increases. The sign of $S$ and the Hall coefficient (Table S2 in the Supplementary Information) is negative, confirming $n$-type carrier transport.

We estimated the carrier concentration ($n$) from the formula $n = 1/eR_H$, where $e$ represents the electronic charge and $R_H$ is the Hall coefficient. The room-temperature $n$ is given in Table 2 and the $R_H$ is given in Table S2 in the Supplementary Information. The Pb$_5$Bi$_6$Se$_{14}$ system was found to have $n$ of $4.8 \times 10^{19}$ cm$^{-3}$, which falls in category of degenerate semiconductor.

As shown in Figure 4(a), the $\sigma$ is highly anisotropic between the in-plane and out-of-plane directions for the whole temperature range measured; for example at 300 K, the in-plane $\sigma$ value (~157 S cm$^{-1}$) is nearly 3.5 times higher than out-of-plane $\sigma$ value (~41.2 S cm$^{-1}$). The $\sigma$ is related to $n$ and the carrier mobility ($\mu$) and is
expressed as:

$$\sigma = en\mu$$  \hspace{1cm} (1)$$

Therefore, the difference in $\sigma$ originates in the difference in $\mu$. The room-temperature $\mu$ was calculated from $n$ and $\sigma$ and are given in Table 2. For Pb$_5$Bi$_6$Se$_{14}$, the in-plane $\mu$ value ($\sim$20 cm$^2$ V$^{-1}$ s$^{-1}$) is nearly 3.5 times higher than out-of-plane $\mu$ value ($\sim$5.4 cm$^2$ V$^{-1}$ s$^{-1}$). The $\mu$ is related to scattering time $\tau$ through the $e$ and $m^*$: $\mu = e\tau/m^*$. Therefore, the low values of $\sigma$ and $\mu$ in out-of-plane direction are principally due to the reduced $\tau$ through the significant electron scattering at the interfaces between PbSe and Bi$_2$Se$_3$ modular layers.

Unlike the $\sigma$, an insensitivity of $S$ to the crystal orientation was observed (Figure 4(b)); for example at 705 K, the in-plane $S$ value ($\sim$210 $\mu$V K$^{-1}$) is in rough agreement with out-of-plane $S$ value ($\sim$230 $\mu$V K$^{-1}$). To interpret the isotropic $S$, we used the following formula as an approximation:\textsuperscript{1,68,69}

$$S = \frac{8\pi^2k_B^2}{3eh^2}m^*T\left(\frac{\pi}{3n}\right)^{\frac{2}{3}},$$  \hspace{1cm} (2)$$

where $h$ is Planck’s constant and $m^*$ is the effective mass. This relationship is derived from the parabolic band model and energy-independent scattering time for metals and degenerate semiconductors. No relationship between $S$ and $\tau$ were found in Eq. (2), resulting in isotropic behaviour in $S$.

Figure 4 (c) shows the temperature dependence of the $\sigmaS^2$ of Pb$_5$Bi$_6$Se$_{14}$ calculated from the measured $\sigma$ and $S$. The highest $\sigmaS^2$ is achieved the in-plane direction, because of the higher $\sigma$ in the in-plane direction and the insensitivity of $S$ to crystal orientation. At 705 K, the in-plane $\sigmaS^2$ value is $\sim$3.0 $\mu$W K$^{-2}$ cm$^{-1}$, which is 47% higher than the out-of-plane $\sigmaS^2$ value ($\sim$1.6 $\mu$W K$^{-2}$ cm$^{-1}$).

Figure 4 (d) shows the temperature dependence of the total thermal conductivity ($\kappa_{\text{total}}$) of the Pb$_5$Bi$_6$Se$_{14}$ sintered compacts in the in-plane and out-of-plane directions. For both directions, the $\kappa_{\text{total}}$ is quite low and is in the range of 0.33–0.58 W K$^{-1}$ m$^{-1}$. The very low value of $\kappa_{\text{total}}$ is of great advantage to further develop high-performance thermoelectric materials.

The electronic thermal conductivity ($\kappa_{\text{el}}$) was estimated using the Wiedemann–Franz relation with the Lorenz number $L = 2.44 \times 10^{-8}$ W $\Omega$ K$^{-2}$ (Sommerfeld value). The lattice thermal conductivity ($\kappa_{\text{lat}}$) was obtained by subtracting $\kappa_{\text{el}}$ from $\kappa_{\text{total}}$ and is plotted in Figure 4 (d). The $\kappa_{\text{lat}}$ is anisotropic between the in-plane
and out-of-plane directions for the whole temperature range measured; for example at 723 K, the in-plane $\kappa_{\text{lat}}$ ($\sim 0.35$ W K$^{-1}$ m$^{-1}$) is $\sim 20\%$ higher than out-of-plane $\kappa_{\text{lat}}$ ($\sim 0.29$ W K$^{-1}$ m$^{-1}$).

The $\kappa_{\text{lat}}$ is related to the average sound velocity ($v_s$), volumetric heat capacity at constant pressure ($C_v$), mean free path of phonon ($l_p$) and is expressed as:

$$\kappa_{\text{lat}} = \frac{1}{3} C_v v_s l_p \quad (3)$$

The $v_s$ is defined as:

$$\frac{1}{v_s^2} = \left[ \frac{1}{3} \left( \frac{1}{v_i^2} + \frac{2}{v_t^2} \right) \right] \quad (4)$$

Table 3 summarizes the room-temperature longitudinal sound velocity ($v_l$), transverse sound velocity ($v_t$) measured by the pulse-echo method, calculated $v_s$, and estimated $l_p$ of Pb$_5$Bi$_6$Se$_{14}$. In this estimation, the $C_v$ was assumed to be equal to measured $C_p$. The in-plane $v_l$ ($\sim 2720$ m s$^{-1}$) and $v_t$ ($\sim 1220$ m s$^{-1}$) are almost same as the out-of-plane $v_l$ ($\sim 2740$ m s$^{-1}$) and $v_t$ ($\sim 1210$ m s$^{-1}$). On the other hand, the out-of-plane $l_p$ (0.6 nm) is shorter than the in-plane $l_p$ (0.8 nm). Moreover, the out-of-plane $l_p$ is $\sim 60\%$ shorter than the length of the $c$-axis (1.604 nm, Table 1) and reach the interlayer distance between PbSe and Bi$_2$Se$_3$ module layers. The facts mean that the extremely low value of the out-of-plane $\kappa_{\text{lat}}$ for Pb$_5$Bi$_6$Se$_{14}$ is attributed to the fact that the interfaces between PbSe layer and Bi$_2$Se$_3$ layer effectively scatter the heat-carrying phonons, like the electron scattering.

The theoretical minimum limit of lattice thermal conductivity ($\kappa_{\text{min}}$) can be written as:

$$\kappa_{\text{min}} = \left( \frac{\pi}{6} \right)^{1/3} k_B n_a^{2/3} \sum v_i \left( \frac{T}{\Theta_i} \right)^2 \int_0^{\Theta_i/T} x^3 e^x \frac{dx}{(e^x - 1)} \quad (5)$$

The $v_i$, $\Theta_i$, and $n_a$ are the sound velocity associated to the longitudinal and transverse modes, Debye temperature associated to these modes, and the number density of atoms, respectively. $\Theta_i$ is related to $v_i$ and $n_a$ and is expressed as:

$$\Theta_i = v_i \left( \frac{h}{k_B} \right) \left( 6 \pi^2 n_a \right)^{1/3} \quad (6)$$

The room-temperature $\kappa_{\text{min}}$ is plotted in Figure 4 (d) and the longitudinal $\Theta_l$ and transverse $\Theta_t$ are shown in Table 3. As shown in Figure 4 (d), the $\kappa_{\text{min}}$ is less than in-plane and out-of-plane $\kappa_{\text{lat}}$. The results suggest that
there is room for reduction in $\kappa_{\text{lat}}$ through increasing complexity of crystal structure/introducing disorder to matrix. This may be achieved by the crystal structural evolution from $[(\text{PbSe})_5][(\text{Bi}_2\text{Se}_3)_3]$ to $[(\text{PbSe})_5][(\text{Bi}_2\text{Se}_3)_6]$ and $[(\text{PbSe})_5][(\text{Bi}_2\text{Se}_3)_9]$.$^{25}$

Figure 5 shows the thermoelectric figure of merit ($ZT$) of the Pb$_5$Bi$_6$Se$_{14}$ sintered compacts in the in-plane and out-of-plane directions calculated from the measured $\sigma$, $S$, and $\kappa_{\text{total}}$. The highest $ZT$ of 0.46 was observed at 705 K for the in-plane direction, because it possesses the highest $\sigma S^2$. The $ZT$ can be further boosted by following strategies; the tuning of $n$ through doping for optimizing $\sigma S^2$, microstructure tuning and single-crystal growth for increasing $\mu$, and crystal structural evolution for reducing $\kappa_{\text{lat}}$.

It is interesting to compare the thermoelectric properties observed in this study with those observed in the previous study.$^{55}$ As shown in Table 4, the $n$ of the sintered sample prepared in this study is lower than that of the melt-grown ingot prepared previously, allowing higher $\sigma S^2$. Moreover, the oriented texture and effective phonon scattering at grain boundaries in the sintered sample lead to lower $\kappa_{\text{lat}}$ and $\kappa_{\text{total}}$. Therefore, the higher $ZT$ was found in the material of this study.

### 3.3 Thermoelectric Properties of Pb$_5$Bi$_6$Se$_6$ and PbBi$_2$S$_4$

Figures 6(a), (b) and (c) and Figures 7(a), (b), and (c) show the temperature dependence of the electrical conductivity ($\sigma$), Seebeck coefficient ($S$), and power factor ($\sigma S^2$) of Pb$_5$Bi$_6$Se$_6$ and PbBi$_2$S$_4$, respectively. The data of both samples are consistent with an $n$-type degenerate semiconductor. The sign of the Hall coefficient confirms the $n$-type carrier transport (Table S2 in Supplementary Information).

As given in Table 2, the room-temperature carrier concentration ($n$) for the Pb$_5$Bi$_6$Se$_6$ and PbBi$_2$S$_4$ samples were found to be $1.2 \times 10^{20} \text{ cm}^{-3}$ and $4.6 \times 10^{19} \text{ cm}^{-3}$, respectively. Like Pb$_5$Bi$_6$Se$_{14}$, the values fall in degenerate semiconductors.

The room-temperature carrier mobilities ($\mu$) were calculated from $n$ and $\sigma$ by using Eq. (1) and are given in Table 2. There are no significant differences observed in $\sigma$ and $\mu$ between the in-plane and out-of-plane directions of Pb$_5$Bi$_6$Se$_6$ and PbBi$_2$S$_4$ for the whole temperature range measured (Figure 6(a) and Figure 7(a)).
For Pb$_3$Bi$_2$S$_6$ at 300 K, the in-plane $\sigma$ (~193 S cm$^{-1}$) and $\mu$ (~9.9 cm$^2$ V$^{-1}$ s$^{-1}$) are slightly less than the out-of-plane $\sigma$ (~219 S cm$^{-1}$) and $\mu$ (~11 cm$^2$ V$^{-1}$ s$^{-1}$). For PbBi$_2$S$_4$ at 300 K, the in-plane $\sigma$ (~68.2 S cm$^{-1}$) and $\mu$ (~9.3 cm$^2$ V$^{-1}$ s$^{-1}$) are slightly less than the out-of-plane $\sigma$ (~89.4 S cm$^{-1}$) and $\mu$ (~12 cm$^2$ V$^{-1}$ s$^{-1}$). Unlike Pb$_5$Bi$_6$Se$_{14}$, the more random textures of Pb$_3$Bi$_2$S$_6$ and PbBi$_2$S$_4$ samples lead to nearly isotropic electrical transport properties.

Like the behavior in $\sigma$, there are no significant differences in $S$ between the in-plane and out-of-plane directions for Pb$_3$Bi$_2$S$_6$ (Figure 6(b)) and PbBi$_2$S$_4$ (Figure 7(b)). For Pb$_3$Bi$_2$S$_6$ at 715 K, the in-plane $S$ (~200 $\mu$V K$^{-1}$) is slightly larger than out-of-plane $S$ value (~180 $\mu$V K$^{-1}$). For PbBi$_2$S$_4$ at 710 K, the in-plane $S$ (~290 $\mu$V K$^{-1}$) is slightly larger than out-of-plane $S$ value (~270 $\mu$V K$^{-1}$).

The $\sigma S^2$ of the Pb$_3$Bi$_2$S$_6$ and PbBi$_2$S$_4$ samples are shown in Figure 6(c) and Figure 7(c), respectively. As a collective property, $\sigma S^2$ also has no significant difference between the in-plane and out-of-plane directions for Pb$_3$Bi$_2$S$_6$ and PbBi$_2$S$_4$. For Pb$_3$Bi$_2$S$_6$, the in-plane $\sigma S^2$ increases with increasing temperature, reaching a maximum of ~2.4 $\mu$W K$^{-2}$ cm$^{-1}$ at 715 K. For PbBi$_2$S$_4$, the out-of-plane $\sigma S^2$ increases from ~1.6 $\mu$W K$^{-2}$ cm$^{-1}$ at 300 K to maximum of ~2.7 $\mu$W K$^{-2}$ cm$^{-1}$ at 610 K and decreases slightly to ~2.6 $\mu$W K$^{-2}$ cm$^{-1}$ at 710 K as the temperature increases. The $\sigma S^2$ for Pb$_3$Bi$_2$S$_6$ and PbBi$_2$S$_4$ is slightly less than the in-plane $\sigma S^2$ for Pb$_3$Bi$_2$Se$_{14}$ (~3.0 $\mu$W K$^{-2}$ cm$^{-1}$ at 705 K, Figure 4(c)).

Figure 6(d) and Figure 7(d) show the temperature dependence of the total thermal conductivity ($\kappa_{\text{total}}$) of Pb$_3$Bi$_2$S$_6$ and PbBi$_2$S$_4$ sintered compacts, respectively, in the in-plane and out-of-plane directions. Like electrical transport properties, the nearly isotropic thermal transport properties were observed for both systems. The sintered compacts of Pb$_3$Bi$_2$S$_6$ and PbBi$_2$S$_4$ show very low value of $\kappa_{\text{total}}$, which is of great advantage as thermoelectric materials. At 723 K, the in-plane $\kappa_{\text{total}}$ was found to be 0.67 W K$^{-1}$ m$^{-1}$ for Pb$_3$Bi$_2$S$_6$ and to be 0.57 W K$^{-1}$ m$^{-1}$ for PbBi$_2$S$_4$.

The electrical thermal conductivity ($\kappa_{\text{el}}$) is estimated using the Wiedemann–Franz relation with the Sommerfeld $L$. The lattice thermal conductivity ($\kappa_{\text{lat}}$) was obtained by subtracting $\kappa_{\text{el}}$ from $\kappa_{\text{total}}$ is plotted in Figure 6(d) for Pb$_3$Bi$_2$S$_6$ and Figure 7(d) for PbBi$_2$S$_4$. Both sintered compacts show extremely low values of $\kappa_{\text{lat}}$, which is less than 0.79 W K$^{-1}$ m$^{-1}$ for Pb$_3$Bi$_2$S$_6$ and less than 0.63 W K$^{-1}$ m$^{-1}$ for PbBi$_2$S$_4$. 


Table 3 summarizes the room-temperature longitudinal sound velocity ($v_l$), transverse sound velocity ($v_t$), average sound velocity ($v_a$), and mean free path of phonon ($l_p$) of Pb$_3$Bi$_2$S$_6$ and PbBi$_2$S$_4$. In the case of all the systems, the in-plane $v_l$ and $v_t$ are almost the same as the out-of-plane $v_l$ and $v_t$. The important point here is that all the $l_p$ are shorter than the length of the c-axes (Table 1) reach the interlayer distances of twin layers in Pb$_3$Bi$_2$S$_6$ and strips in PbBi$_2$S$_4$. These results suggest that the extremely low values of $\kappa_{lat}$ are attributed to the interfaces between twin layers in Pb$_3$Bi$_2$S$_6$ or strips in PbBi$_2$S$_4$ which effectively scatter the heat-carrying phonons.

The room-temperature $\kappa_{\text{min}}$ is plotted in Figure 4(d) and the longitudinal $\Theta_l$ and transverse $\Theta_t$ are shown in Table 3. The $\kappa_{\text{min}}$ is less than the in-plane and out-of-plane $\kappa_{\text{lat}}$, suggesting a possibility for further reduction of $\kappa_{\text{lat}}$. Like Pb$_5$Bi$_6$Se$_{14}$, future reduction in $\kappa_{\text{lat}}$ through increasing complexity of crystal structure is probably achieved by the crystal structural evolution (for example, layered structure built up from Pb$_3$Bi$_2$S$_6$ to Pb$_8$Bi$_9$S$_{23}$). \cite{23,26}

Figure 8 and Figure 9 show the thermoelectric figure of merit ($ZT$) of the Pb$_3$Bi$_2$S$_6$ and PbBi$_2$S$_4$ sintered compacts in the in-plane and out-of-plane directions calculated from the measured $\sigma$, $S$, and $\kappa_{\text{total}}$, respectively. There are no significant differences in $ZT$ between the in-plane and out-of-plane directions for both samples. For Pb$_3$Bi$_2$S$_6$, the in-plane $ZT$ increases with increasing temperature, reaching a maximum of 0.26 at 715 K. For PbBi$_2$S$_4$, the out-of-plane $ZT$ increases from 0.08 at 300 K to maximum of 0.33 at 710 K as the temperature increases. The $ZT$ values of Pb$_3$Bi$_2$S$_6$ and PbBi$_2$S$_4$ are lower than that for Pb$_5$Bi$_6$Se$_{14}$ (Figure 4(c)), because of lower $\sigma S^2$ and higher $\kappa_{\text{total}}$. Like Pb$_5$Bi$_6$Se$_{14}$, the $ZT$ of Pb$_3$Bi$_2$S$_6$ and PbBi$_2$S$_4$ can be further improved by the tuning of n through doping for optimizing $\sigma S^2$, microstructure tuning and single-crystal growth for increasing $\mu$, and crystal structural evolution for reducing $\kappa_{\text{lat}}$.

Finally, as this paper was being reviewed a narrow gap semiconductor Pb-Bi$_4$Se$_{11}$ was reported to crystallize in the monoclinic space group $C2/m$ (a member of the lillianite series) possessing a very low thermal conductivity ($\sim$0.33 W m$^{-1}$ K$^{-1}$ at 300 K). This adds to the collection of compounds described here and points to the Pb-Bi-Q (Q =S, Se, Te) class as a promising set of potentially important thermoelectric materials. \cite{76}
3.4 Comparison between Pb$_5$Bi$_6$Se$_{14}$, Pb$_3$Bi$_2$S$_6$ and PbBi$_2$S$_4$

Finally, we compare the thermoelectric properties of Pb$_5$Bi$_6$Se$_{14}$ with those of Pb$_3$Bi$_2$S$_6$ and PbBi$_2$S$_4$. In the Pb$_5$Bi$_6$Se$_{14}$ sintered compacts, the $c$-plane was preferentially oriented parallel to the out-of-plane direction, resulting in highly anisotropic electrical and thermal transport properties. The in-plane $\sigma S^2$ is higher than the out-of-plane $\sigma S^2$, because of the higher $\sigma$ in the in-plane direction and the insensitivity of $S$ to crystal orientation. Moreover, the in-plane $\kappa_{\text{lat}}$ is higher than out-of-plane $\kappa_{\text{lat}}$. Because of higher $\sigma S^2$ in the in-plane direction, the highest $ZT$ of 0.46 was observed at 705 K for the in-plane direction.

The crystal grains of Pb$_3$Bi$_2$S$_6$ and PbBi$_2$S$_4$ were grown randomly, leading to nearly isotropic electrical and thermal transport properties in the sintered compacts. There are no significant differences observed in $\sigma S^2$, $\kappa_{\text{lat}}$, and $ZT$ between the in-plane and out-of-plane directions for the whole temperature range measured. The $ZT$ values increase with increasing temperature, reaching a maximum of 0.26 at 715 K for in-plane direction in Pb$_3$Bi$_2$S$_6$ and 0.33 at 710 K for the out-of-plane direction in PbBi$_2$S$_4$. The $ZT$ values of Pb$_3$Bi$_2$S$_6$ and PbBi$_2$S$_4$ are lower than that for Pb$_5$Bi$_6$Se$_{14}$, because of lower $\sigma S^2$ and higher $\kappa_{\text{total}}$.

4. Concluding remarks

We investigated for the first time the high-temperature thermoelectric properties of the cannizzarite homologous member Pb$_5$Bi$_6$Se$_{14}$, lillianite homologous member Pb$_3$Bi$_2$S$_6$, and galenobismuthite homologous member PbBi$_2$S$_4$. The layered structures of these systems yield very low lattice thermal conductivity in the range of 0.30 to 0.81 W K$^{-1}$ m$^{-1}$ over the temperature range of 300 to 723 K, because the interfaces between layers effectively scatter the heat-carrying phonons. Moreover, all samples are $n$-type degenerate semiconductors. The very low lattice thermal conductivity and degenerate semiconductor-like behavior are of great advantages to further develop high-performance thermoelectric materials. The highest thermoelectric figure of merit $ZT$ of 0.46 at
705 K was observed for Pb$_5$Bi$_6$Se$_{14}$ in the in-plane direction. Future reduction in $\kappa_{\text{int}}$ through increasing complexity of crystal structure is probably achievable by the crystal structural evolution enabled by the homologous series. The thermoelectric power factor can also be further boosted by tuning carrier concentration through doping and increasing carrier mobility through microstructure tuning and single-crystal growth.

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Supplementary Information

The sintered mass density, room-temperature Hall coefficient, thermal diffusivity, heat capacity, and scanning electron microscopy micrographs of Pb$_5$Bi$_6$Se$_{14}$, Pb$_3$Bi$_2$S$_6$, and PbBi$_2$S$_4$ are available.

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Notes

The authors declare that they have no competing financial interests.

Author Contributions
M.O. and M.G.K. designed the project. M.O. and D.Y.C synthesized the samples. M.O. and M.K. sintered the samples, performed the XRD and SEM experiments, and investigated the electrical and thermal properties. M.O. D.Y.C, and M.G.K. analyzed the results and wrote the manuscript.
References


[72] Y.-L. Pei, J.Q. He, J.-F. Li, F. Li, Q. Liu, W. Pan, C. Barreteau, D. Berardan, N. Dragoe and L.-D. Zhao, 


press*, DOI: 10.1021/ic501327u.
Figure 1.

Crystal structures of (a) a member of the cannizzarite homologous series Pb$_5$Bi$_6$Se$_{14}$, (b) a member of the lillianite homologous series Pb$_3$Bi$_2$S$_6$, and (c) a member of the galenobismuthite series PbBi$_2$S$_4$. Size of atoms in this figure is arbitrary for better view.
Figure 2.

Powder X-ray diffraction (XRD) patterns for (a) Pb$_5$Bi$_6$Se$_{14}$, (b) Pb$_3$Bi$_2$S$_6$, and (c) PbBi$_2$S$_4$ before sintering and after sintering and out-of-plane XRD patterns of the sintered compacts. The sintered compacts were hand-ground to measure the powder XRD patterns. References are taken from Ref.45 for Pb$_5$Bi$_6$Se$_{14}$, Ref.51 for Pb$_3$Bi$_2$S$_6$, and Ref.54 for PbBi$_2$S$_4$. 
Figure 3.

Scanning electron microscopy micrographs of the fractured section for the sintered compacts of (a) Pb$_5$Bi$_6$Se$_{14}$, (b) Pb$_3$Bi$_2$S$_6$, and (c) PbBi$_2$S$_4$. The disk-type samples (~15 mm diameter × ~2 mm thickness) were fractured parallel to the pressing direction.
Temperature dependence of the (a) electrical conductivity ($\sigma$), (b) Seebeck coefficient ($S$), (c) power factor ($\sigma S^2$), and (d) total thermal conductivity ($\kappa_{\text{total}}$) for the sintered compacts of Pb$_5$Bi$_6$Se$_{14}$ measured perpendicular (in-plane) and parallel (out-of-plane) to the pressing direction. The lattice thermal conductivity ($\kappa_{\text{lat}}$) and theoretical minimum limit of lattice thermal conductivity ($\kappa_{\text{min}}$) are also plotted in (d).
Figure 5.

Temperature dependence of the thermoelectric figure of merit ($ZT$) for the sintered compacts of Pb$_5$Bi$_6$Se$_{14}$ perpendicular (in-plane) and parallel (out-of-plane) to the pressing direction.
Figure 6.

Temperature dependence of the (a) electrical conductivity ($\sigma$), (b) Seebeck coefficient ($S$), (c) power factor ($\sigma S^2$), and (d) total thermal conductivity ($\kappa_{\text{total}}$) for the sintered compacts of Pb$_3$Bi$_2$S$_6$ measured perpendicular (in-plane) and parallel (out-of-plane) to the pressing direction. The lattice thermal conductivity ($\kappa_{\text{lat}}$) and theoretical minimum limit of lattice thermal conductivity ($\kappa_{\text{min}}$) are also plotted in (d).
Figure 7.

Temperature dependence of the (a) electrical conductivity ($\sigma$), (b) Seebeck coefficient ($S$), (c) power factor ($\sigma S^2$), and (d) total thermal conductivity ($\kappa_{\text{total}}$) for the sintered compacts of PbBi$_2$S$_4$ measured perpendicular (in-plane) and parallel (out-of-plane) to the pressing direction. The lattice thermal conductivity ($\kappa_{\text{lat}}$) and theoretical minimum limit of lattice thermal conductivity ($\kappa_{\text{min}}$) are also plotted in (d).
Figure 8.

Temperature dependence of the thermoelectric figure of merit ($ZT$) for the sintered compacts of Pb$_3$Bi$_2$S$_6$ perpendicular (in-plane) and parallel (out-of-plane) to the pressing direction.
Figure 9.

Temperature dependence of the thermoelectric figure of merit ($ZT$) for the sintered compacts of PbBi$_2$S$_4$ perpendicular (in-plane) and parallel (out-of-plane) to the pressing direction.
Table 1.

Lattice parameters calculated from powder XRD patterns of Pb$_5$Bi$_6$Se$_{14}$, Pb$_3$Bi$_2$Se$_6$, and PbBi$_2$S$_4$ before and after sintering.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Lattice parameter</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb$_5$Bi$<em>6$Se$</em>{14}$ before sintering</td>
<td>$a = 2.1537$ nm, $b = 0.4202$ nm, $c = 1.6028$ nm, $\beta = 97.34^\circ$</td>
</tr>
<tr>
<td>Pb$_5$Bi$<em>6$Se$</em>{14}$ after sintering</td>
<td>$a = 2.1540$ nm, $b = 0.4206$ nm, $c = 1.6047$ nm, $\beta = 97.39^\circ$</td>
</tr>
<tr>
<td>Ref. [54]</td>
<td>$a = 2.15689(3)$ nm, $b = 0.420148(4)$ nm, $c = 1.60096(3)$ nm, $\beta = 97.537(1)^\circ$</td>
</tr>
<tr>
<td>Pb$_3$Bi$_2$Se$_6$ before sintering</td>
<td>$a = 0.4116$ nm, $b = 1.3571$ nm, $c = 2.0679$ nm</td>
</tr>
<tr>
<td>Pb$_3$Bi$_2$Se$_6$ after sintering</td>
<td>$a = 0.4119$ nm, $b = 1.3576$ nm, $c = 2.0663$ nm</td>
</tr>
<tr>
<td>Ref. [61]</td>
<td>$a = 0.4111(1)$ nm, $b = 1.3540(4)$ nm, $c = 2.0654(4)$ nm</td>
</tr>
<tr>
<td>PbBi$_2$S$_4$ before sintering</td>
<td>$a = 1.1789$ nm, $b = 0.4088$ nm, $c = 1.4572$ nm</td>
</tr>
<tr>
<td>PbBi$_2$S$_4$ after sintering</td>
<td>$a = 1.1812$ nm, $b = 0.4085$ nm, $c = 1.4568$ nm</td>
</tr>
<tr>
<td>Ref. [64]</td>
<td>$a = 1.1753$ nm, $b = 0.4087$ nm, $c = 1.4612$ nm</td>
</tr>
</tbody>
</table>
Table 2.

Room-temperature carrier concentration \((n)\) and carrier mobility \((\mu)\) of the sintered compacts of \(\text{Pb}_5\text{Bi}_6\text{Se}_{14}\), \(\text{Pb}_3\text{Bi}_2\text{S}_6\), and \(\text{PbBi}_2\text{S}_4\).

<table>
<thead>
<tr>
<th>Sample</th>
<th>(n) (cm(^{-3}))</th>
<th>(\mu) (cm(^2) V(^{-1}) s(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{Pb}_5\text{Bi}<em>6\text{Se}</em>{14})</td>
<td>(4.8 \times 10^{19})</td>
<td>20</td>
</tr>
<tr>
<td>in-plane</td>
<td></td>
<td></td>
</tr>
<tr>
<td>out-of-plane</td>
<td></td>
<td>5.4</td>
</tr>
<tr>
<td>(\text{Pb}_3\text{Bi}_2\text{S}_6)</td>
<td>(1.2 \times 10^{20})</td>
<td>11</td>
</tr>
<tr>
<td>in-plane</td>
<td></td>
<td>9.3</td>
</tr>
<tr>
<td>out-of-plane</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(\text{PbBi}_2\text{S}_4)</td>
<td>(4.6 \times 10^{19})</td>
<td>12</td>
</tr>
<tr>
<td>in-plane</td>
<td></td>
<td></td>
</tr>
<tr>
<td>out-of-plane</td>
<td></td>
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Table 3.

Room-temperature longitudinal sound velocity ($v_l$), transverse sound velocity ($v_t$), average sound velocity ($v_a$), mean free path of phonon ($l_p$), and Debye temperature associated with the longitudinal ($\Theta_l$) and transverse modes ($\Theta_t$) of the sintered compacts of Pb$_5$Bi$_6$Se$_{14}$, Pb$_3$Bi$_2$S$_6$, and PbBi$_2$S$_4$.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$v_l$ (m s$^{-1}$)</th>
<th>$v_t$ (m s$^{-1}$)</th>
<th>$v_a$ (m s$^{-1}$)</th>
<th>$l_p$ (nm)</th>
<th>$\Theta_l$ (K)</th>
<th>$\Theta_t$ (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb$_5$Bi$<em>6$Se$</em>{14}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>in-plane</td>
<td>2720</td>
<td>1220</td>
<td>1380</td>
<td>0.8</td>
<td>260</td>
<td>120</td>
</tr>
<tr>
<td>out-of-plane</td>
<td>2740</td>
<td>1210</td>
<td>1370</td>
<td>0.6</td>
<td>270</td>
<td>120</td>
</tr>
<tr>
<td>Pb$_3$Bi$_2$S$_6$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>in-plane</td>
<td>3160</td>
<td>1590</td>
<td>1780</td>
<td>0.9</td>
<td>320</td>
<td>160</td>
</tr>
<tr>
<td>out-of-plane</td>
<td>3090</td>
<td>1580</td>
<td>1770</td>
<td>0.7</td>
<td>310</td>
<td>160</td>
</tr>
<tr>
<td>PbBi$_2$S$_4$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>in-plane</td>
<td>3240</td>
<td>1780</td>
<td>1980</td>
<td>0.6</td>
<td>330</td>
<td>180</td>
</tr>
<tr>
<td>out-of-plane</td>
<td>3210</td>
<td>1770</td>
<td>1970</td>
<td>0.6</td>
<td>330</td>
<td>180</td>
</tr>
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</table>
Table 4.

Room-temperature thermoelectric properties of the sintered sample of Pb$_5$Bi$_6$Se$_{14}$ observed in this study and the melt-grown ingot of Pb$_5$Bi$_6$Se$_{14}$ observed in the previous study.

<table>
<thead>
<tr>
<th>Direction</th>
<th>$n$ (cm$^{-3}$)</th>
<th>$\sigma$ (S cm$^{-1}$)</th>
<th>$S$ ($\mu$V K$^{-1}$)</th>
<th>$\sigma S$ ($\mu$W K$^{-2}$ cm$^{-1}$)</th>
<th>$\kappa_{\text{total}}$ (W K$^{-1}$ cm$^{-1}$)</th>
<th>$\kappa_{\text{lat}}$ (W K$^{-1}$ cm$^{-1}$)</th>
<th>$ZT$</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>In-plane</td>
<td>4.8 × 10$^{19}$</td>
<td>157</td>
<td>88</td>
<td>120</td>
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<td>0.48</td>
<td>0.06</td>
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</tr>
<tr>
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<td>100</td>
<td>41</td>
<td>0.40</td>
<td>0.37</td>
<td>0.03</td>
<td>0.03</td>
<td>This study</td>
</tr>
<tr>
<td>Unknown</td>
<td>8.6 × 10$^{19}$</td>
<td>454</td>
<td>28</td>
<td>36</td>
<td>1.0</td>
<td>0.72</td>
<td>0.01</td>
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**Graphical abstract**

We demonstrate a notable power factor and an extremely low lattice thermal conductivity in Pb$_5$Bi$_6$Se$_{14}$, a member of the cannizzarite homologous series; Pb$_3$Bi$_2$S$_6$, a member of the lillianite homologous series; and PbBi$_2$S$_4$, a member of the galenobismuthite series.