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# Thermoelectric properties of polycrystalline *n*-type $\text{Pb}_5\text{Bi}_6\text{Se}_{14}$

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## ABSTRACT

Chalcogenides are currently focusing attention due to their interesting thermoelectric properties that stem from their complex crystal structures and semiconducting properties. Herein, we report on the synthesis and measurements of the transport properties in a broad temperature range (2 – 723 K) of polycrystalline *n*-type  $\text{Pb}_5\text{Bi}_6\text{Se}_{14}$ , a member of the homologous series  $(\text{PbSe})_5(\text{Bi}_2\text{Se}_3)_{3m}$  ( $m = 1$ ), to assess its thermoelectric potential and to shed light on the basic mechanisms governing the low-temperature transport. The anisotropic crystal structure gives rise to transport properties that differ on samples measured parallel or perpendicular to the pressing direction. The measurements show that this compound exhibits semiconducting-like properties with thermopower values that reach  $250 \mu\text{V K}^{-1}$  at 723 K. The lattice thermal conductivity values are very low in the whole temperature range ( $\sim 0.5 \text{ W m}^{-1} \text{ K}^{-1}$ ) and close to the theoretical minimum thermal conductivity estimated from sound velocities. Thanks to this remarkable property, a peak  $ZT$  of 0.5 is achieved at 720 K.

## INTRODUCTION

Since the discovery of thermoelectric effects, thermoelectricity has continued to generate strong interest for both fundamental and industrial aspects. Among the renewable energy sources studied, thermoelectricity may be an interesting alternative for harvesting the large amounts of waste heat in our environment and directly converting it into electrical energy. The efficiency of a thermoelectric material is evaluated by the dimensionless thermoelectric figure of merit  $ZT$  which depends, at a given absolute temperature  $T$ , on three transport coefficients: the Seebeck coefficient (or thermopower)  $\alpha$ , the electrical resistivity  $\rho$  and the total thermal conductivity  $\kappa$  and is given by the relation  $ZT = \alpha^2 T / \rho \kappa$  [1,2]. Materials with high  $ZT$  values ( $\geq 1$ ) and capable of operating in the widest temperature range are currently intensively sought [3].

Homologous series of compounds provide an ideal playground to design novel thermoelectric materials [4,5]. Homologies are series of crystal structures that are composed of similar building blocks whose number increases by regular increments. These structural characteristics allow for a relatively easy manipulation of the physical properties through a controlled modification of the crystal structure and/or chemical composition. In particular, such tunable structural complexity offers an interesting way to reach extremely low lattice thermal conductivity.

Among the homologous series investigated so far from a thermoelectric point of view, the series  $[(\text{PbSe})_5][(\text{Bi}_2\text{Se}_3)_3]_m$  with  $m = 1, 2, 3$  has recently been identified as promising thermoelectric compounds that can harbor non-trivial topological properties for  $m = 2$  [6-11]. These compounds crystallize into monoclinic structures (space group  $P2_1/m$  and  $C2/m$  for  $m = 1$  and  $m = 2$ , respectively [10-13]) that contain a large number of atoms. The crystal structure of the  $m = 1$  member, namely  $\text{Pb}_5\text{Bi}_6\text{Se}_{14}$ , was described by Zhang *et al.* [12] (Figure 1). The

structure consists in  $m$  layers of  $\text{Bi}_2\text{Se}_3$  interacting via van der Waals gaps and sandwiched by adjacent bilayers of  $\text{PbSe}$ . High-temperature thermoelectric properties of  $\text{Pb}_5\text{Bi}_6\text{Se}_{14}$  have been recently reported by Ohta *et al.* [6]. This investigation revealed that this compound behaves as an  $n$ -type semiconductor and shows very low thermal conductivity values of the order of 0.3 and 0.6  $\text{W m}^{-1} \text{K}^{-1}$  in the in-plane and out-of-plane directions, respectively. This favorable combination led to a maximum  $ZT$  of 0.47 at 705 K in the out-of-plane direction [6]. Further attempts at manipulating the physical properties of the  $m = 1$  and  $m = 2$  compounds were realized through partial substitutions of Ag and Cu for Pb, resulting in a superconducting transition at 1.7 K in the Ag-containing  $m = 1$  compound [11].

Herein, we report on the synthesis and structural and chemical characterizations of polycrystalline  $\text{Pb}_5\text{Bi}_6\text{Se}_{14}$  by means of powder X-ray diffraction and scanning electron microscopy. We further extended the measurements of the transport properties down to liquid-helium temperatures. These results confirm that  $\text{Pb}_5\text{Bi}_6\text{Se}_{14}$  exhibits semiconducting-like properties with very low thermal conductivity that mimics glassy systems leading to a peak  $ZT$  of 0.5 at 720 K. Our experimental findings show that this compound should be amenable to interesting thermoelectric properties when appropriately doped.

## EXPERIMENTAL DETAILS

### Synthesis

The polycrystalline  $\text{Pb}_5\text{Bi}_6\text{Se}_{14}$  sample was synthesized by a two-step synthesis method. As a first step, the two precursors  $\text{PbSe}$  and  $\text{Bi}_2\text{Se}_3$  were prepared by weighting stoichiometric amounts of high-purity elemental powders (Pb 99.99 %, Se 99.999 %, and Bi 99.995 %). The stoichiometric mixture of these elements was loaded into quartz tubes of 18 mm outer

diameter and 16 mm inner diameter. The tubes were evacuated under secondary vacuum to a pressure of  $\sim 10^{-6}$  Pa and then sealed under vacuum. The tubes were heated to 773 K at a rate of  $\sim 40$  K h<sup>-1</sup>, then heated to 1393 K at a rate of  $\sim 80$  K h<sup>-1</sup> and held at this temperature for 12 h before being cooled to room temperature over 2 h. In a second step, both precursors were hand-ground into fine powders and mixed in stoichiometric amounts in order to obtain Pb<sub>5</sub>Bi<sub>6</sub>Se<sub>14</sub>. The mixture was cold-pressed into cylindrical pellets, which were annealed at 873 K for ten days according to the PbSe – Bi<sub>2</sub>Se<sub>3</sub> phase diagram [14]. After a final quenching, the pellets were ground into fine powders and consolidated by spark plasma sintering (SPS) in a graphite die under a pressure of 80 MPa for 16 min. The density of the cylindrical pellet, estimated from weight and geometrical dimensions, was higher than 98% of the theoretical density from crystallographic data.

### **Structural and Chemical Characterizations**

Phase purity of the precursors and final compound were examined by powder X-ray diffraction (PXRD) using a Bruker D8 Advance diffractometer with CuK $\alpha_1$  radiation ( $\lambda = 1.54056$  Å). The chemical homogeneity and spatial distribution of the elements were studied by scanning electron microscopy (SEM) and X-ray elemental mapping using a Quanta 650 FEG (FEI). The chemical composition of the sample was determined by electron probe microanalysis (EPMA) on a JEOL JXA 8500F microprobe using PbTe, Bi and SnSe as standards to determine the Pb, Bi and Se concentrations, respectively.

### **Transport properties measurements**

For transport properties measurements, the dense cylindrical pellet was cut into bars, coins and squares with appropriate sizes both perpendicular and parallel to the pressing direction

(Figure 2a). The Seebeck coefficient and electrical resistivity were measured simultaneously with a ZEM-3 system (ULVAC-RIKO) over the temperature range 300 – 723 K. The total thermal conductivity was determined in the same temperature range from the thermal diffusivity ( $a$ ), the specific heat ( $C_p$ ) and the experimental density ( $d$ ) using the relation  $\kappa = aC_p d$ .  $a$  and  $C_p$  were measured by a laser flash method (LFA 427, Netzsch) and a differential scanning calorimeter (Pegasus 403 F3, Netzsch), respectively. In the present case, we have neglected the temperature dependence of  $d$ . Electrical resistivity, thermopower and thermal conductivity were measured simultaneously between 5 and 300 K using the thermal transport option of a physical property measurement system (PPMS, Quantum Design). The Hall coefficient  $R_H$  was measured in the temperature range 5 – 300 K by a five-point method using the AC (alternating current) transport option of the PPMS. As a first approximation, the electron concentration  $n$  was estimated by using the single-band relation  $n = 1/R_H e$  where  $e$  is the elementary charge. The Hall mobility  $\mu_H$  was calculated by  $\mu_H = R_H/\rho$ . The combined experimental uncertainty in the determination of the  $ZT$  values is estimated to be 17% [15].

## RESULTS AND DISCUSSIONS

### Structural and chemical characterizations

The strongly anisotropic crystal structure of  $\text{Pb}_5\text{Bi}_6\text{Se}_{14}$  gives rise to some preferred orientation of the grains. More specifically, the  $c$ -axis is preferentially oriented along the pressing direction resulting in a strong renormalization of the intensities of the  $(00l)$  reflections. Nevertheless, the PXRD patterns collected before and after the sintering process could be fully indexed within the space group  $P2_1/m$  of  $\text{Pb}_5\text{Bi}_6\text{Se}_{14}$  indicating no evident thermal decomposition (Figure 2b). These results further suggest the absence of any

secondary phases, which was confirmed by a careful analysis of the sample by SEM in backscattered electron mode (Figure 3) used to contrast the main phase from possible secondary phases. X-ray elemental mapping indicated a homogeneous distribution of Pb, Bi and Se within the sample (see Figure 3). EPMA experiments further confirmed the phase-pure nature of the sample and showed that the actual chemical composition ( $\text{Pb}_{4.96}\text{Bi}_{6.03}\text{Se}_{14.01}$ ) does not differ from the nominal composition to within experimental uncertainty.

### Transport Properties

Figure 4a shows the electrical resistivity as a function of the temperature. As anticipated, the texture observed in the PXRD data leads to anisotropic  $\rho$  values. The anisotropy between the perpendicular and parallel directions remains nearly temperature-independent with  $\rho$  values lower in the perpendicular direction. At low temperatures,  $\rho$  increases with temperature before decreasing from 300 to 500 K where a minimum is achieved. Upon further warming,  $\rho$  increases up to 650 K before eventually decreasing at higher temperatures. The relatively high  $\rho$  values are typical of heavily-doped semiconductors. Yet, the complex temperature dependence points to non-trivial evolution of the charge carrier properties with temperature. Hall effect measurements performed below room temperature revealed a dominant electron-like signal in the whole temperature range indicative of electrons as the main charge carriers. We note that, in principle, the monoclinic crystal structure should lead to tensor galvanomagnetic properties making the Hall coefficient  $R_H$  dependent on crystalline orientation. In the present case, measurements performed in the parallel and perpendicular directions showed a negligible anisotropy (see Figure 4b), which justifies the approximations used herein. At 300 K, the Hall coefficient  $R_H$  corresponds to an electron concentration of  $4 \times 10^{19} \text{ cm}^{-3}$  that remains nearly constant upon cooling (Figure 4c).

The room-temperature  $R_H$  value yields electron Hall mobilities  $\mu_H$  of the order of 5 and 12  $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$  in the parallel and perpendicular direction, respectively. The temperature dependence of the Hall mobility, shown in Figure 4d, indicates a complicated behavior.  $\mu_H$  tends to slightly decrease with increasing temperature in both directions. This trend may be an indication that both scattering by neutral impurities ( $\mu_H = cst$ ) and by acoustic phonons ( $\mu_H \propto T^{-3/2}$ ) are present.

$\text{Pb}_5\text{Bi}_6\text{Se}_{14}$  exhibits negative thermopower values (Figure 4e) consistent with the Hall effect data.  $\alpha$  increases monotonically (in absolute values) with increasing temperature to reach  $-215$  and  $-230 \mu\text{V K}^{-1}$  at 700 K in the perpendicular and parallel directions, respectively, both values being in excellent agreement with those measured by Ohta *et al* [6]. Unlike  $\rho$ ,  $\alpha$  does not show any significant dependence on the direction to within experimental uncertainty. Above 600 K, the tendency of  $\alpha(T)$  to saturate is likely a sign of thermal excitation of minority carriers across the band gap. A rough estimation of the band gap  $E_g$  width may be obtained from the maximum  $\alpha_{max}$  value and the temperature at which this maximum occurs  $T_{max}$  according to the relation  $E_g = 2e\alpha_{max}T_{max}$ . This simple approximation yields an estimated band gap of 0.33 eV.

Figure 5a displays the temperature dependence of the total thermal conductivity of  $\text{Pb}_5\text{Bi}_6\text{Se}_{14}$  in the parallel and perpendicular directions. The values measured, ranging between 0.4 and 0.5  $\text{W m}^{-1} \text{K}^{-1}$  at 720 K, are extremely low and similar to those observed in several other chalcogenides [16-25]. At low temperatures,  $\kappa$  does not show a well-defined dielectric maximum akin to glassy compounds. Because the samples are textured, the thermal conductivity is expected to be anisotropic with lower values along the parallel direction due to the layered crystal structure and the effect of applied pressure during the sintering process. Our experimental data are in good agreement with this expectation for  $T > \sim 25$  K. Below this temperature, the anisotropy vanishes.



The lattice thermal conductivity  $\kappa_L$  was obtained by subtracting the electronic thermal conductivity  $\kappa_e$  from  $\kappa$  (Figure 5b). The former contribution has been estimated using the Wiedemann–Franz law  $\kappa_e = LT/\rho$  where  $L$  is the Lorenz. An estimation of  $L$  has been obtained following the approach used in Ref. 26 yielding a value of  $1.95 \times 10^{-8} \text{ V}^2 \text{ K}^{-2}$  at 300 K. This value leads to an electronic contribution that only amounts to 4% of the total thermal conductivity at 300 K due to the relatively high  $\rho$  values. The very low  $\kappa_L$  values (Figure 5b) may be attributed to the significant structural disorder as well as to the interfaces between PbSe and Bi<sub>2</sub>Se<sub>3</sub> layers that contribute to lowering the  $\kappa$  values in the parallel direction. Interestingly, these values are close to the theoretical minimum thermal conductivity  $\kappa_{min}$  estimated using the high-temperature limit of the expression developed by Cahill and Pohl [27]

$$\kappa_{min} = \frac{1}{2} \left( \frac{\pi}{6} \right)^{1/3} k_B V^{-2/3} (2v_S + v_L)$$

where  $k_B$  is the Boltzmann constant,  $V$  is the atomic volume and  $v_S$  and  $v_L$  are the transverse and longitudinal sound velocities.  $v_S$  and  $v_L$  were measured by a pulse-echo method and found to be 2580 and 1290 m s<sup>-1</sup>, respectively, in good agreement with those measured by Ohta *et al.* [6]. These values yield  $\kappa_{min} \approx 0.25 \text{ W m}^{-1} \text{ K}^{-1}$  above 300 K.

As shown in Figure 5c, the combination of these favorable transport properties results in  $ZT$  values that increase with increasing temperature to reach a maximum  $ZT$  of 0.5 at 720 K in the perpendicular direction. The anisotropies observed in the  $\rho$  and  $\kappa$  data cancel out yielding nearly isotropic  $ZT$  values. This result contrast with the findings of Ohta *et al.* who obtained anisotropic  $ZT$  values. This discrepancy mainly originates from differences in the electrical resistivity, both the thermopower and thermal conductivity values being in good agreement. We surmise that this difference can be due to differences in the microstructure of the samples,

variations in texture possibly affecting the mobilities of the charge carriers.

## CONCLUSION

Dense polycrystalline sample of  $\text{Pb}_5\text{Bi}_6\text{Se}_{14}$  has been successfully prepared by annealing a mixture of  $\text{PbSe}$  and  $\text{Bi}_2\text{Se}_3$  precursors at high temperatures followed by SPS. PXRD, SEM and EPMA analyses showed no traces of secondary phases and an excellent correlation between the nominal and actual compositions. The layered and complex crystal structure of  $\text{Pb}_5\text{Bi}_6\text{Se}_{14}$  gives rise to anisotropic transport properties and very low lattice thermal conductivity that decreases from 0.8 to 0.4  $\text{W m}^{-1} \text{K}^{-1}$  above 300 K. These results show that the thermal transport is efficiently disrupted and close to the minimum thermal conductivity estimated from the measured sound velocities. This feature is the key ingredient that yields a peak  $ZT$  value of 0.5 at 720 K. These encouraging results show that  $\text{Pb}_5\text{Bi}_6\text{Se}_{14}$  may be an interesting platform to achieve good thermoelectric performances thanks to its remarkable thermal transport.

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## FIGURE CAPTIONS

Fig. 1. View of the crystal structure of  $\text{Pb}_5\text{Bi}_6\text{Se}_{14}$  projected along the  $b$  axis. The blue dashed lines represent the monoclinic unit cell. The Bi-Se layers (shown in purple) are separated by one PbSe layer (shown in grey). The large black spheres correspond to Pb atoms, the purple spheres to Bi atoms and the smaller green spheres to Se atoms. In this structure, the Pb, Bi and Se atoms are distributed over five, six and fourteen distinct crystallographic sites, respectively. In this figure, the different sites for a given element are not distinguished.

Fig. 2. Comparison of the experimental PXRD patterns of  $\text{Pb}_5\text{Bi}_6\text{Se}_{14}$  collected before and after SPS. The vertical green bars correspond to the expected Bragg reflections.

Fig. 3. SEM backscattered electron images collected on the  $\text{Pb}_5\text{Bi}_6\text{Se}_{14}$  sample along with the corresponding elemental X-ray maps indicating a good chemical homogeneity of the sample.

Fig. 4. (a) Temperature dependence of the electrical resistivity of  $\text{Pb}_5\text{Bi}_6\text{Se}_{14}$  measured in the perpendicular and parallel directions. Hall coefficient  $R_H$  (b), Hall electron concentration  $n$  (c) and Hall mobility  $\mu_H$  (d) as a function of temperature. Error bars represent 10% measurement uncertainty. (e) Temperature dependence of the thermopower of  $\text{Pb}_5\text{Bi}_6\text{Se}_{14}$  measured in the perpendicular and parallel directions. In panels (b), (c) and (d), the color-coded symbols are similar to those in panel (a).

Fig. 5. Total (a), electronic and lattice (b) thermal conductivities of  $\text{Pb}_5\text{Bi}_6\text{Se}_{14}$  measured parallel and perpendicular to the pressing direction. Data measured between 270 and 300 K are not shown due to the thermal radiations, which further explain the slight discrepancy between the data measured at low and high temperatures. (c)  $ZT$  as a function of temperature for  $\text{Pb}_5\text{Bi}_6\text{Se}_{14}$ .