Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Enhanced thermoelectric performance of InTe through Pb doping

Shantanu Misra[1], Adèle Léon[1], Petr Levinský[2], Jiří Hejtmánek[2], Bertrand Lenoir[1,*], Christophe Candolfi[1,*]

[1] *Institut Jean Lamour, UMR 7198 CNRS – Université de Lorraine, Campus ARTEM, 2 allée André Guinier, BP 50840, 54011 Nancy, France*

[2] *FZU – Institute of Physics of the Czech Academy of Sciences, Cukrovarnická 10/112, 162 00, Prague 6, Czech Republic*

[*]Corresponding authors: christophe.candolfi@univ-lorraine.fr; bertrand.lenoir@univ-lorraine.fr

Content

6). Equations of the Klemens-Callaway model of alloy scattering and **Fig S11** showing the theoretical dependence of κ_L.

7). Equations of the SPB model to calculate the hole concentration dependence of the *ZT* values.

8). Fig S12. Measurements performed on a second sample doped with x = 0.1% Pb.

1). Schematic view of the samples cut parallel and perpendicular to the pressing direction for transport property measurements.

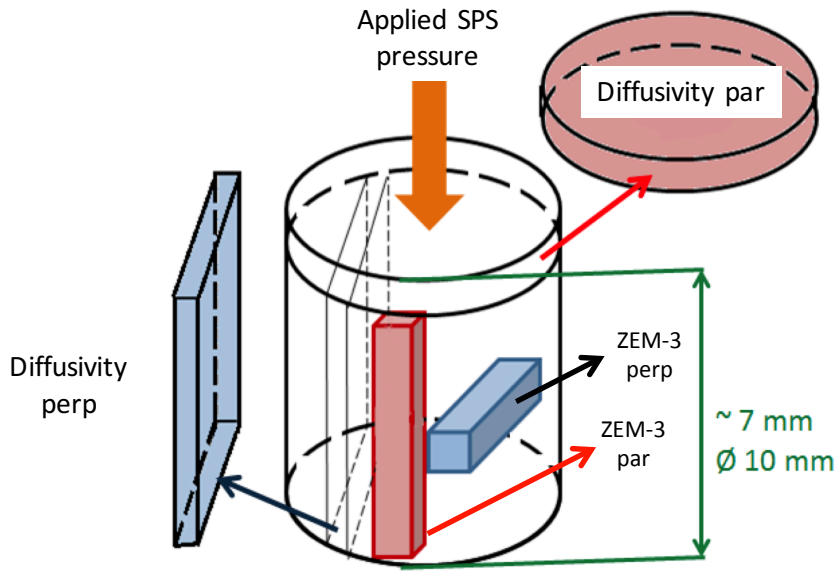

Fig S1. Schematic view of samples cut parallel and perpendicular to the pressing direction from the pellet consolidated by SPS.

2). Comparison of the transport properties measured parallel and perpendicular to the pressing directions.

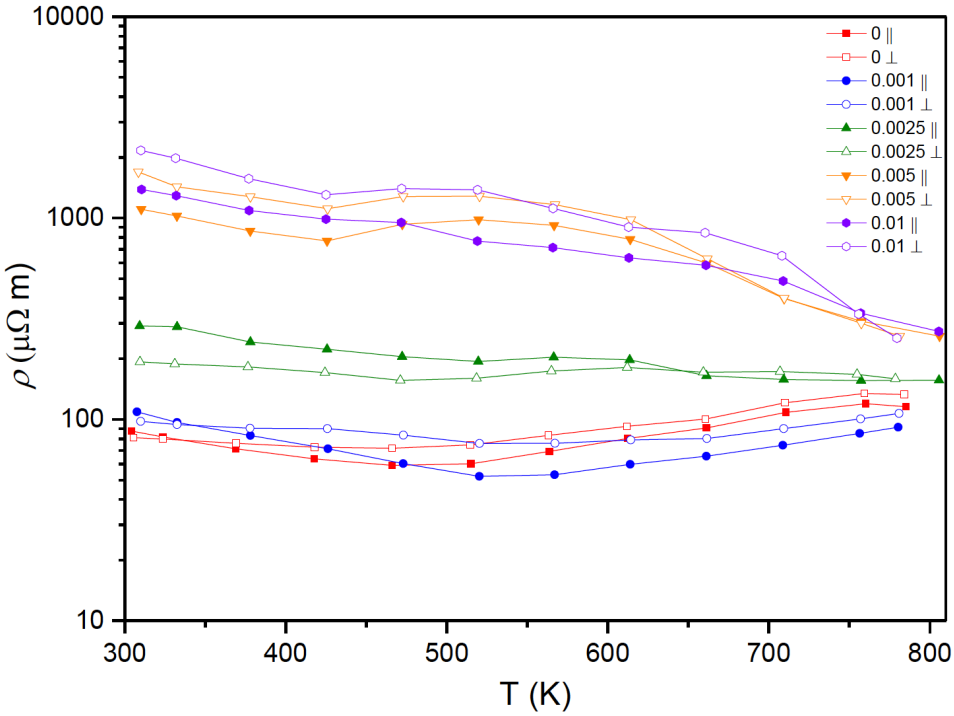

Fig S2. Temperature dependence of the electrical resistivity ρ measured parallel (filled symbols) and perpendicular (open symbols) to the pressing direction for the x = 0.0, 0.10, 0.25, 0.50 and 1% Pb-doped samples.

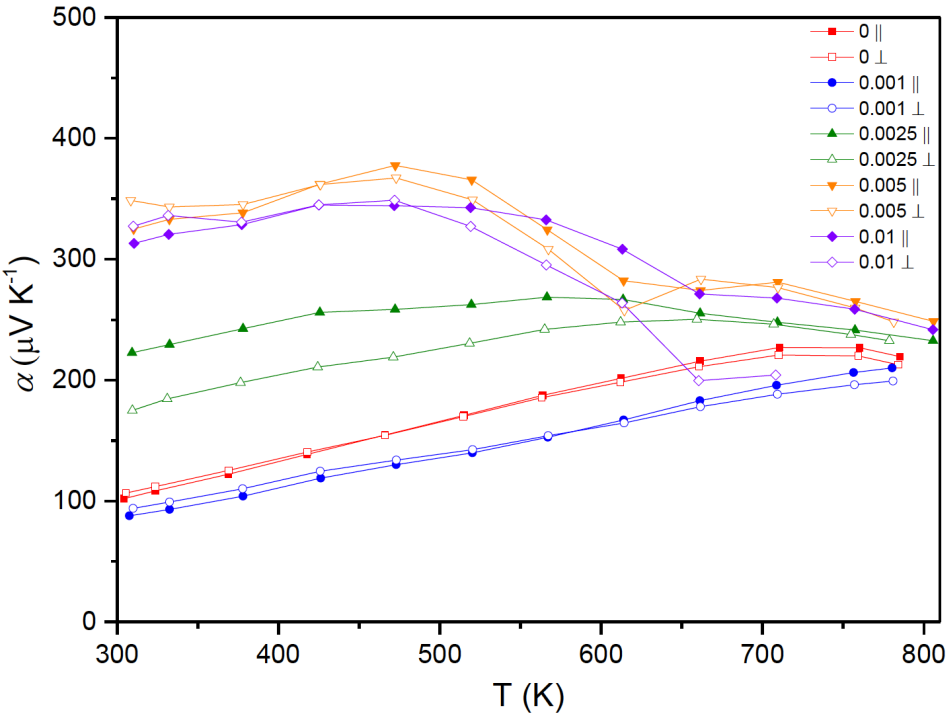

Fig S3. Temperature dependence of the thermopower α measured parallel (filled symbols) and perpendicular (open symbols) to the pressing direction for the x = 0.0, 0.10, 0.25, 0.50 and 1% Pb-doped samples.

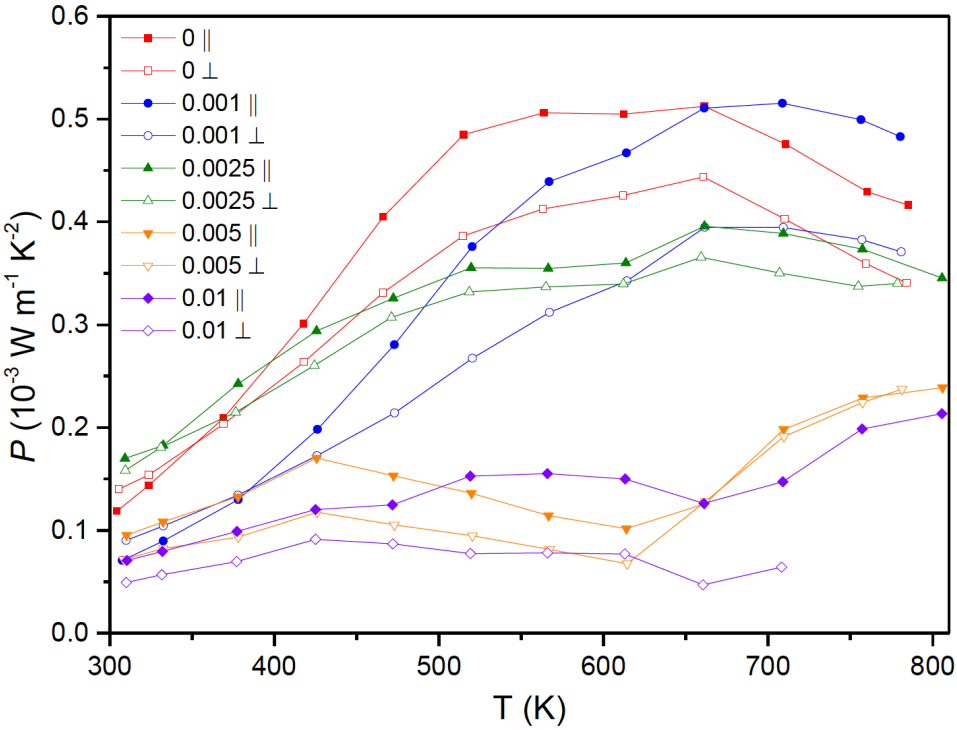

Fig S4. Temperature dependence of the power factor $PF = \alpha^2/\rho$ measured parallel (filled symbols) and perpendicular (open symbols) to the pressing direction for the x = 0.0, 0.10, 0.25, 0.50 and 1% Pb-doped samples.

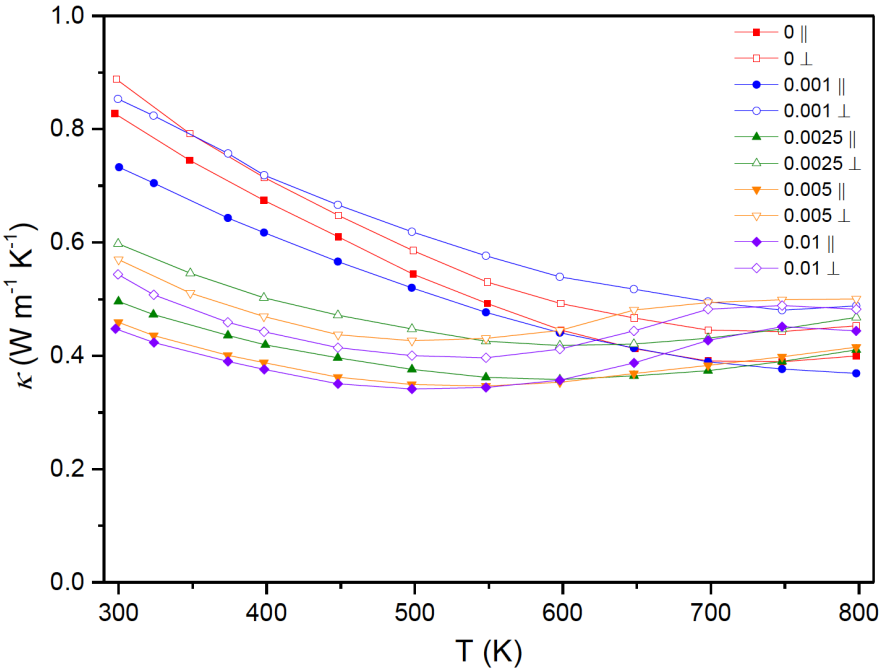

Fig S5. Temperature dependence of the total thermal conductivity κ measured parallel (filled symbols) and perpendicular (open symbols) to the pressing direction for the x = 0.0, 0.10, 0.25, 0.50 and 1% Pb-doped samples.

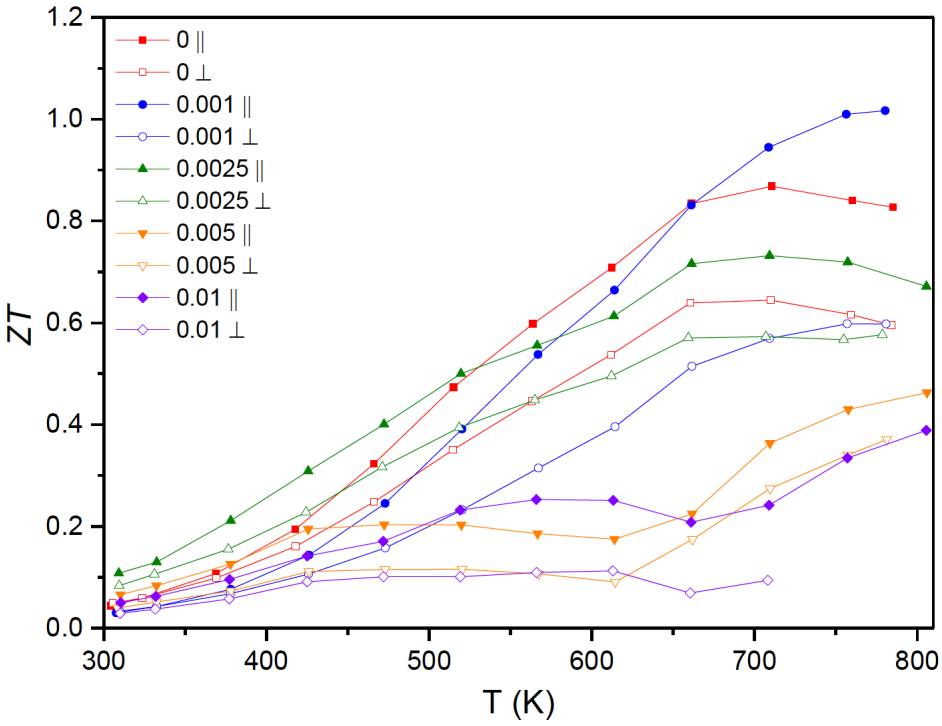

Fig S6. Temperature dependence of the dimensionless thermoelectric figure of merit *ZT* measured parallel (filled symbols) and perpendicular (open symbols) to the pressing direction for the x = 0.0, 0.10, 0.25, 0.50 and 1% Pb-doped samples.

3). SEM images and their corresponding elemental X-ray maps of the x = 0.5 and 1% samples.

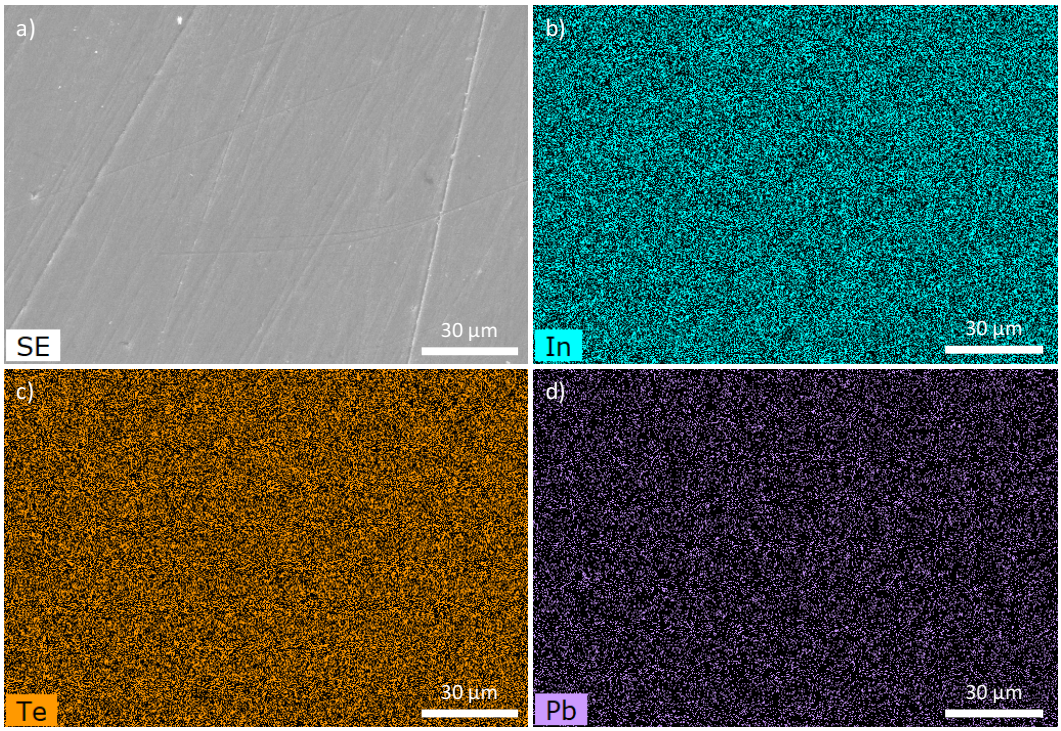

Fig S7. SEM image and its corresponding elemental X-ray maps of the 0.5% Pb-doped sample.

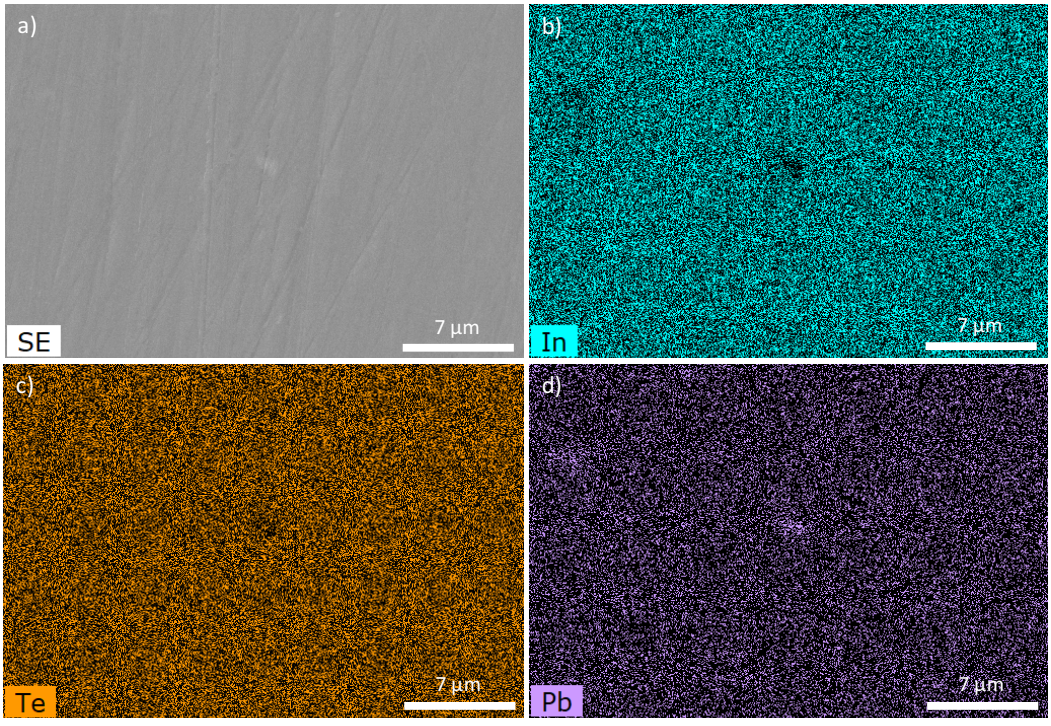

Fig S8. SEM image and its corresponding elemental X-ray maps of the 1% Pb-doped sample.

4). Variation in the unit cell volume V as a function of the Pb concentration x_{Pb} at 300 K.

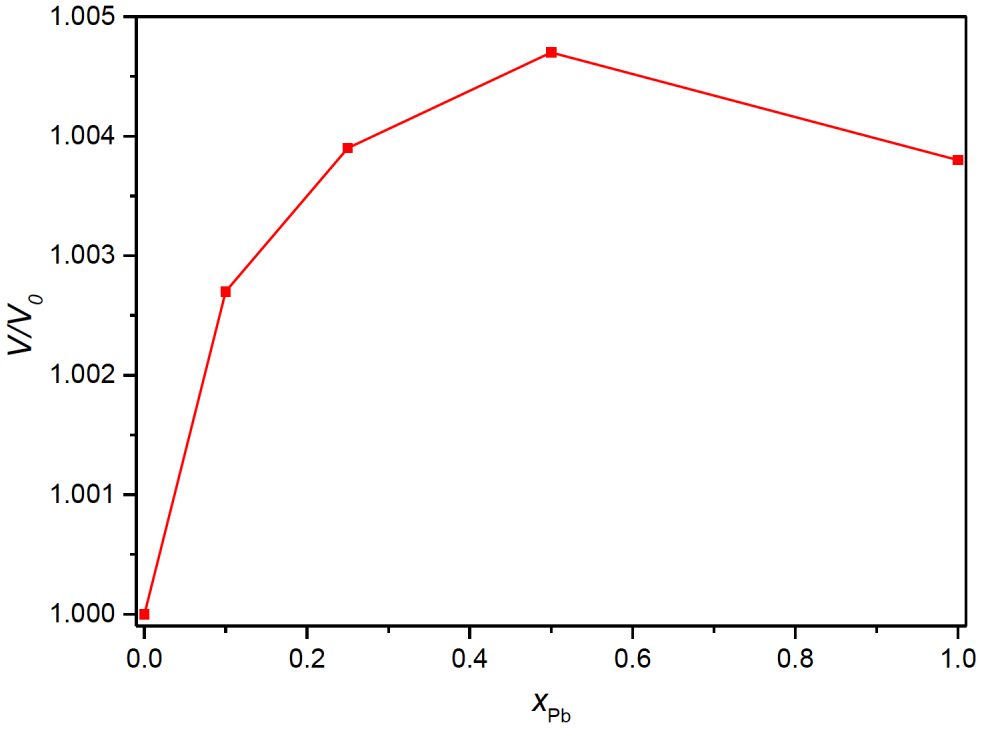

Fig S9. Variation in the unit cell volume V as a function of the Pb concentration x_{Pb} at 300 K (given in %) for the $In_{1-x}Pb_xTe$ series. V has been normalized to the volume of the $x = 0.0$ sample denoted V_0.

5). Temperature dependence of the Lorenz number calculated by a single parabolic band model with acoustic phonon scattering.

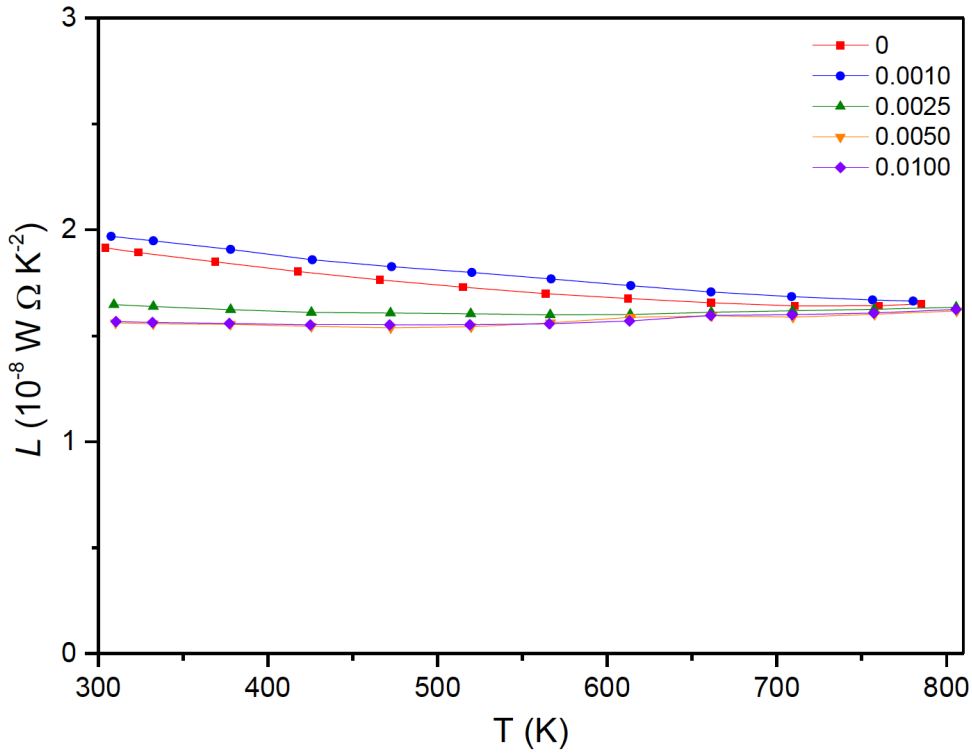

Fig S10. Temperature dependence of the Lorenz number calculated by a single parabolic band model with acoustic phonon scattering.

6). Equations of the Klemens-Callaway model of alloy scattering

Within the Klemens-Callaway model of alloy scattering, the relation between the lattice thermal conductivity of the alloyed samples ($\kappa_{L,alloy}$) and that of the pure compound ($\kappa_{L,pure}$) is the following (Refs. 37 to 39 in the main text):

$$\frac{\kappa_{L,alloy}}{\kappa_{L,pure}} = \frac{\arctan(u)}{u}$$

$$u^2 = \frac{\pi\theta_D\Omega}{2\hbar v^2}\kappa_{ph,pure}\Gamma$$

where Ω is the volume per atom, Γ is the scattering parameter, θ_D is the Debye temperature (169 K for InTe) and v is the average experimental speed of sound (1903 m s^{-1}). Γ can be defined as:

$$\Gamma = x(1-x)\left[\left(\frac{\Delta M}{M}\right)^2 + \varepsilon\left(\frac{\Delta a}{a}\right)^2\right]$$

where M is the molar mass of each composition, a is the lattice parameter, and ΔM and Δa are the difference of each quantity between the alloy and the pure compounds. Although the parameter ε can be related to the Grüneisen parameter and elastic properties, an experimental determination of its value is challenging. For this reason, ε is usually treated as a fitting parameter. Following this approach, a value of 200 is required to describe the decrease in κ_L observed at 300 K as a function of the Pb concentration. While this value is higher than that

typically considered for PbTe in the literature ($\varepsilon \approx 65$),[1] a similar value has been inferred, for instance, for the Zintl phase solid solution $Ca_5Al_{2-x}In_xSb_6$ ($\varepsilon \approx 150$).[2]

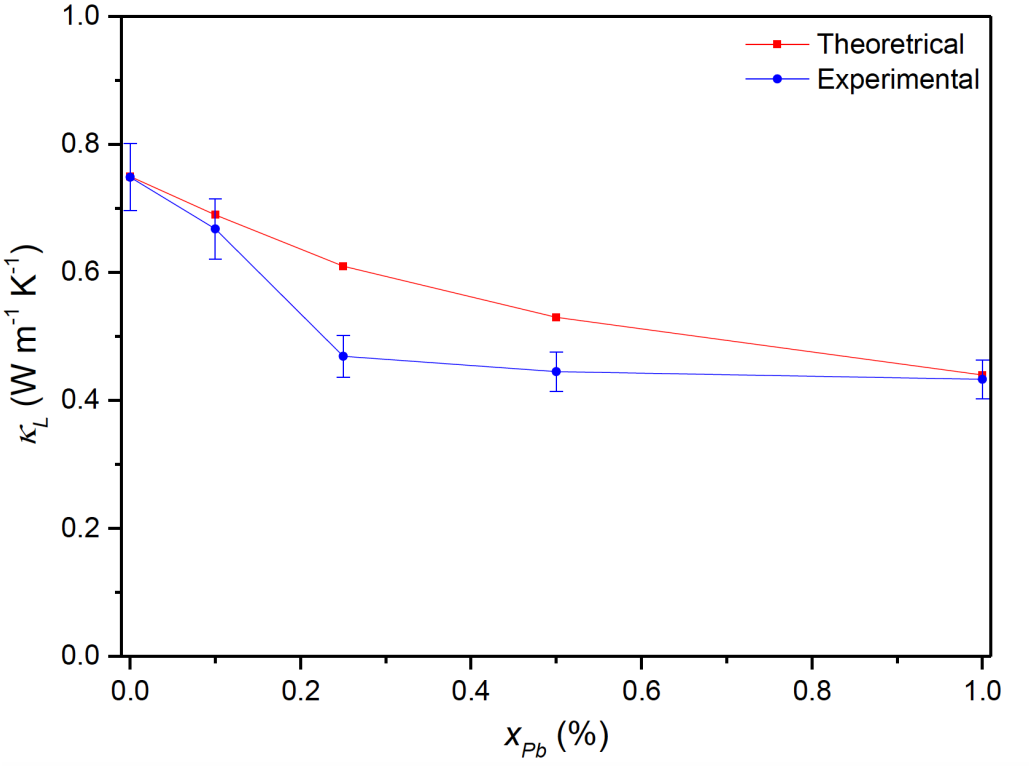

Fig S11. Lattice thermal conductivity κ_L at 300 K as a function of the Pb content expressed in %. The theoretical dependence has been calculated from the above-mentioned Klemens-Callaway model of alloy scattering.

7). Equations of the SPB model to calculate the hole concentration dependence of the *ZT* values

Within a single parabolic band model, the hole concentration dependence of the *ZT* values can be calculated using the following expressions (Ref. 36 in the main text)

$$ZT = \frac{\alpha^2}{L + (\psi\beta)^{-1}}$$

$$\beta = \frac{\mu_0 (m^*_{DOS}/m_e)^{3/2} T^{5/2}}{\kappa_L}$$

$$\psi = 2e\left(\frac{2\pi k_B m_e}{h^2}\right)^{3/2} \frac{F_\lambda(\eta)}{\Gamma(1+\lambda)}$$

where m_e is the bare electron mass, e is the elementary charge, k_B is the Boltzmann constant, h is the Planck constant, μ_0 is the intrinsic charge carrier mobility and $\Gamma(x)$ is the gamma function. $F_\lambda(\eta)$ is the Fermi integral defined as

$$F_\lambda(\eta) = \int_0^\infty \frac{\xi^\lambda d\xi}{1 + e^{\xi - \eta}}$$

where ξ is the reduced energy of the charge carriers. Acoustic phonon scattering ($\lambda = 0$) was assumed to be the dominant scattering mechanism across the entire Pb concentration range. μ_0 was determined from the Hall mobility μ_H

$$\mu_H = \mu_0 \frac{\sqrt{\pi} F_\lambda(\eta)}{2\Gamma(1+\lambda) F_{1/2}(\eta)}$$

The κ_L value measured at 750 K for the x = 0.1% sample was used and considered constant across the entire Pb concentration range. In this model, density-of-states effective masses of 0.98 and $0.86m_e$, intrinsic mobilities μ_0 of 10 and 12 $cm^2\ V^{-1}\ s^{-1}$ and lattice thermal conductivities of 0.28 and 0.22 $W\ m^{-1}\ K^{-1}$ were considered for InTe and the Pb-doped samples respectively. The κ_L value measured at 750 K for the x = 0.1% sample was considered constant across the entire Pb concentration range, despite some variations with x are observed experimentally. This hypothesis explains the discrepancy observed between the theoretical curve and some of the experimental points.

References

[1] H. Wang, A. D. LaLonde, Y. Pei and G. J. Snyder, *Adv. Funct. Mater.*, 2012, **23**, 1586–1596.

[2] A. Zevalkink, J. Swallow, S. Ohno, U. Aydemir, S. Bux and G. J. Snyder, *Dalton Trans.*, 2014, **43**, 15872–15878.

8). Measurements performed on a second sample doped with x = 0.1% Pb

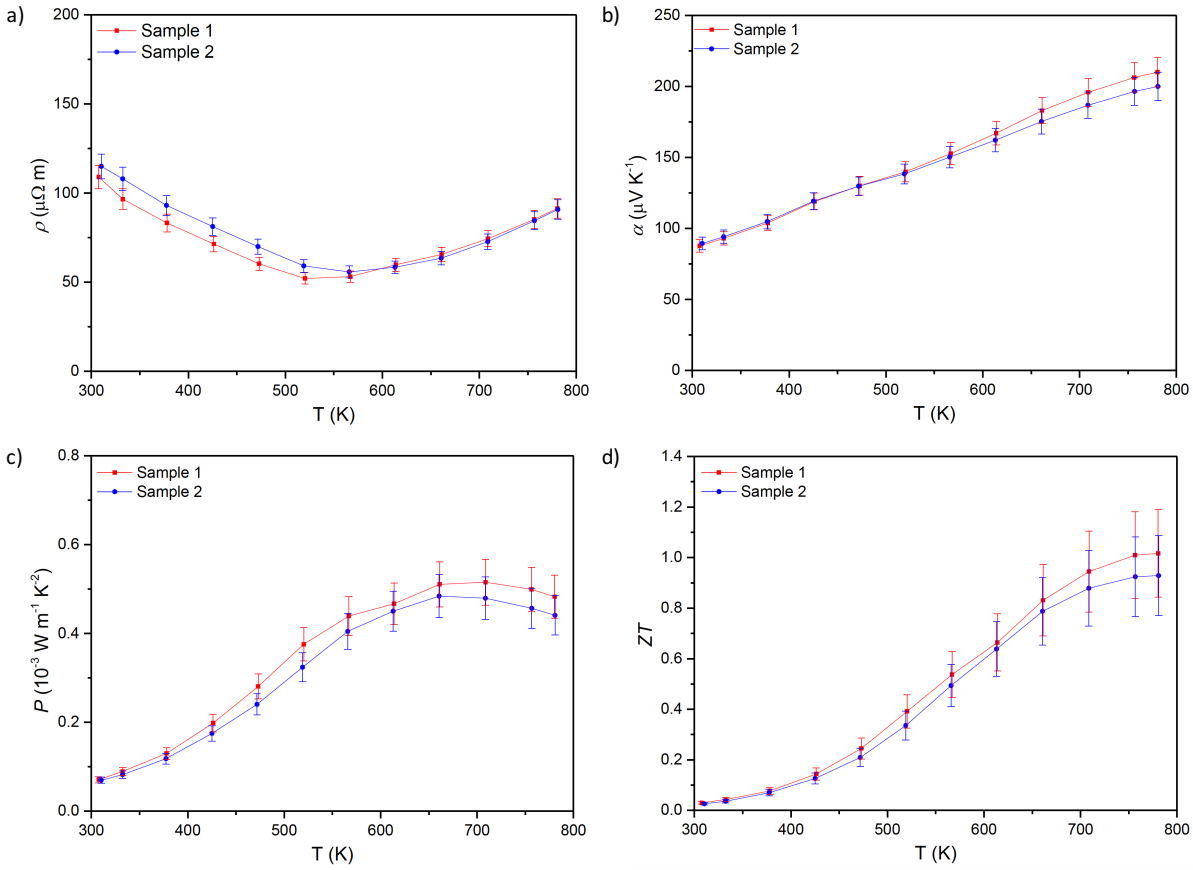

Fig S12. Temperature dependences of the a) electrical resistivity ρ, b) thermopower α, c) power factor P and d) dimensionless thermoelectric figure of merit ZT measured parallel to the pressing direction on the x = 0.1% sample discussed in the main manuscript (sample 1) and on a second sample (sample 2) showing the good reproducibility of these measurements to within experimental uncertainty (represented by the error bars).