

Supporting Information for

Seeing Is Believing: Weak Phonon Scattering from Nanostructures in alkali metal doped Lead Telluride

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Experimental Procedure

$\text{Pb}_{1-y}\text{A}_y\text{Te}$ ($\text{A}=\text{Na}, \text{K}, \text{Rb}, \text{Cs}$ $y\%$, $y=1, 1.25, 2.5$), and $\text{Pb}_{0.9875-y}\text{K}_{0.0125}\text{Na}_y\text{Te}$ (PbTe-K 1.25 % - Na $y\%$, $y=0.4, 0.6, 0.8, 1.0, 1.2, 1.4$) specimens were produced by direct reaction of high-purity metals (American Elements Pb 99.99%, 5N Plus Te 99.999%, Aldrich $\text{K}>99.95\%$, Aldrich $\text{Na}>99.95\%$) as starting materials. In a typical procedure approximately 10 mg of A (per 10 g of product) were first loaded in a carbon coated silica tube inside a glove box under nitrogen atmosphere. Subsequently, appropriate quantities of Pb and Te were back-calculated and added in the tube, which was evacuated to a base pressure of 10^{-4} Torr and fused

All reactions took place in a box furnace by Lindberg. The furnace was fired at 1050 °C over 12 h and soaked at that temperature for 4 h followed by a rapid cooling to room temperature over a period of 3 h. The samples were examined with powder X-ray diffraction and scanning electron microscopy along with measurements of their electrical and thermal transport properties.^[1]

The electrical conductivity and Seebeck coefficient were determined simultaneously in the temperature range $300 \leq T \leq 700$ K in a ULVAC ZEM-3 variable temperature system. A Netzsch LFA 457 instrument was utilized to measure the thermal diffusivity of disk-shaped specimens in the same temperature regime. The heat capacity of samples was determined in the same instrument based on a comparative method relative to a standardized Pyroceram 9606 reference having the same geometry and similar physical dimensions with the loaded samples. Subsequently, the total thermal conductivity was calculated using the relation $\kappa_{\text{tot}} = \alpha C_p \delta$, where α is thermal diffusivity, C_p is specific heat, and δ is density of the sample, calculated from sample dimensions and mass in units of g/cm^3 .

The thin sections of the specimens were examined under transmission electron microscopy (TEM) mode with JEOL 2100F transmission electron microscopes. TEM samples were prepared by conventional methods, with due care to mechanical and ion beam damage. The samples were cut into 3mm-diameter discs by disc cutter, then ground, dimpled, polished, and subsequently Ar-ion milled on a stage cooled with liquid nitrogen. High-resolution images were simulated with the MacTempas program code with the following parameters as input: Spherical aberration of 1 mm, defocus spread of 8 nm, semiconvergence angle of illumination of 0.55 mrad, and a 7 nm^{-1} diameter of the objective lens' aperture.

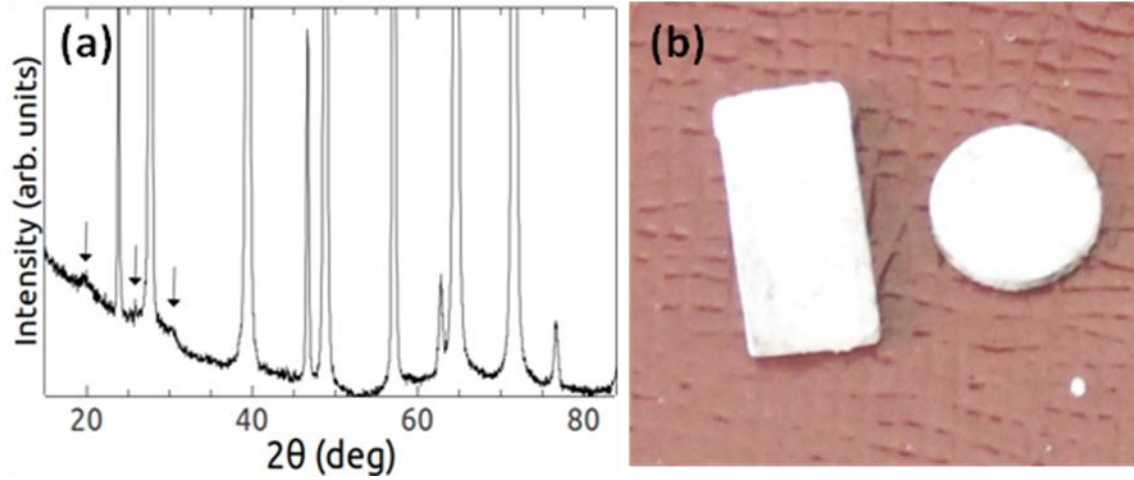


Figure S1 (a) X-ray data of PbTe-Cs 1%, the arrows indicate secondary phases like Pb.(b) A typical PbTe-Cs 1% pair of specimens used in studies of thermoelectric heavy oxidation (white discoloration) develops within hours of air exposure.

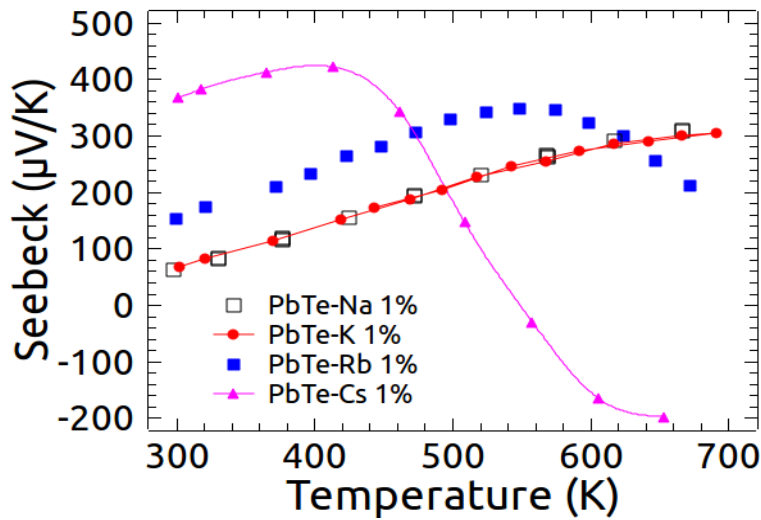


Figure S2: Seebeck coefficient as a function of temperature for PbTe-A 1% (A= Na, K, Rb, Cs). Notice that bipolar effects setting in at 550 K for PbTe-Rb 1% ($\sim 5 \times 10^{18} \text{ cm}^{-3}$) evidence that not all Rb is entering the lattice as a dopant in contrast to PbTe-Na 1% and PbTe-K 1%. The PbTe-Cs 1% data indicate a very low p-type carrier concentration suggesting that Cs does not dope the PbTe lattice significantly. The above is a clear indication that not all alkali metals are appropriate p-type dopants for PbTe.

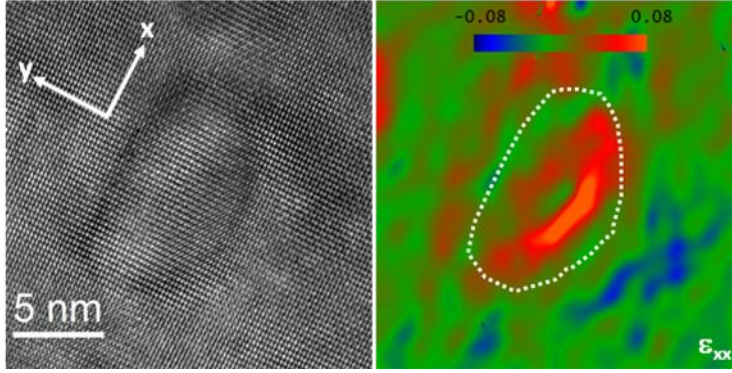


Figure S3 Lattice image and strain map of PbTe-K 1.25%-Na 0.6% show no strain at the interface between the precipitate and matrix.

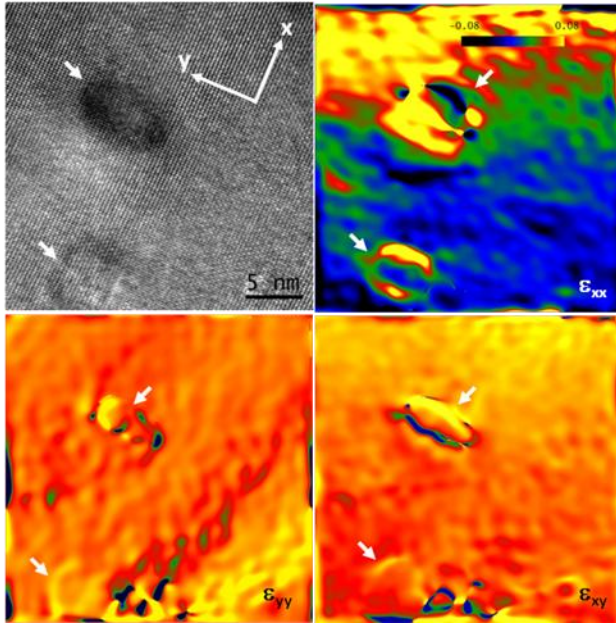


Figure S4 Lattice image and strain maps of two precipitates in sample PbTe-Na 2.5 % show dislocations and strain at the interface between the precipitates and matrix.

Lorenz number calculations

In order to better approximate the Lorenz number in p-type PbTe we have followed the Boltzmann transport equation formalism within the relaxation time approximation. This is

considered a standardized way of treating transport properties in narrow band gap systems. Furthermore, we have taken into account the peculiarities of the valence band structure of PbTe.

The valence band structure of PbTe consists of two sub-bands with very different effective masses [6]. The primary valence band has a much lighter mass. The two bands are close in energy in the temperature regime 300-500 K and hence the chemical potential can access states both from the light and heavy valence band with increased doping. Generally, for doping levels $> 6 \times 10^{19} \text{ cm}^{-3}$ it is accepted that the two bands model is more appropriate [6]. Therefore Lorenz number calculations were divided in two parts:

A. Light doping

In this regime a single valence band presumably dominates transport and acoustic phonon scattering is more appropriate to apply. A good approximation that helps define more accurately the Lorenz number was described by Fitts. [2] The method consists of expressing the measured thermoelectric power and L number as a function of Fermi integrals of the reduced chemical potential, η . The fit of the thermopower yields a unique value of η at each temperature that is subsequently fed into the expression for L which is then used to generate values of κ_e through the Wiedemann-Franz law. Application of the method holds remarkably well for a diverse set of semiconducting materials [3, 4, 5].

B. Heavy doping

Under heavy doping conditions a strong interaction between the light (l) and heavy (h) valence sub-bands is expected. Therefore, an increased lattice thermal conductivity appears as a result of the Lorenz number being actually higher than the metallic limit [6]. In such a case an appropriate scattering time model has to take into account carriers transferring from one band to the other, changing their momentum (the l band lies in the $\langle 111 \rangle$ direction and h band in the $\langle 100 \rangle$ direction in the first Brillouin zone). Kolomoets has solved, in a generic fashion, the problem of two interacting parabolic bands with one having a much higher effective mass assuming again an energy independent scattering time that depends on band overlap. [7].

Within this framework explicit relations for the thermoelectric power and Lorenz number can be found:

$$S = -\frac{k_B}{e} \frac{I_2 + \mu^* I_1}{I_1 + \mu^* I_0} \quad (1)$$

$$L_B = \frac{\kappa_e}{(\frac{k}{e})^2 \sigma T} = \frac{I_3 I_1 - I_0^2 + \mu^* (I_3 I_0 - I_1 I_2) + \mu^{*2} (I_2 I_0 - I_1^2)}{(I_1 + \mu^* I_0)^2} \quad (2)$$

where I_n are generalized integrals of the form:

$$I_n = \int_{-\gamma}^{-\infty} x^n \Delta(x) dx + \int_{-\gamma}^{\infty} \frac{x^n \Delta(x) dx}{1 + \beta^* (\frac{x+\gamma}{x+\mu^*})^{1/2}} \quad (3)$$

In equations 1-3 κ_B is the Boltzman constant, μ^* is the dimensionless, thermal energy normalized chemical potential, x is the reduced chemical potential, γ is the energy difference of the chemical potential from the top of the heavy valence band normalized by the thermal energy, β is a dimensionless quantity expressing the probability of transition between the bands and is proportional to $\sim(m_h/m_l)^{3/2}$ where $m_{h,l}$ are the effective masses of the respective bands(h for heavy, l for light) and Δ is a function of x .

The region of application of the above model is limited both by temperature and doping [6], thus it has been applied for PbTe-Na 2.5% and PbTe-K 1.25%-Na 0.6% specimens in Figure 5 of the manuscript for temperatures close to 300 K only. Generally, this model leads to higher Lorenz numbers than the metallic limit, e.g. $2.59 \times 10^{-8} \text{ W}\Omega\text{K}^{-2}$ for PbTe-K 1.25%-Na 0.6% at room temperature. The full details of the model will be developed in a separate publication [8]. For all other temperatures the acoustic phonon scattering model was found to be adequate. The acoustic phonon model was also applied for PbTe-K 1.25% and PbTe-Na 1.25% samples, in Figure 5 of the manuscript, at all temperatures.

References

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