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

Electronic Supplementary Information

High thermoelectric performance of slight Sb doped PbTe alloys

Tingting Chen[1], Kaiqi Zhang[1], Hongchao Wang[1,2*], Wenbin Su[1], Fahad Mehmood[1], Teng Wang[1], Jinze Zhai[1], Xue Wang[1], Taichang Huo[1], Chunlei Wang[1#]

1. School of Physics, State Key Laboratory of Crystal Materials, Shandong University, Jinan, China.

2. State Key Laboratory of Metastable Materials Science and Technology, Yanshan University, Qinhuangdao, China.

* E-mail: wanghc@sdu.edu.cn (H. Wang)

E-mail: wangcl@sdu.edu.cn (C. Wang)

Defect formation energy calculation. Defect formation energy was calculated using the density functional theory (DFT) method via the Vienna ab initio simulation package (VASP). A method combining the projector augmented wave (PAW) method with the generalized gradient approximation of Perdew-Burke and Ernzerhof (GGA-PBE) was applied. A plane wave cutoff energy of 500 eV, an electronic convergence criterion of 10^{-5} eV, and the Monkhorst-Pack method with 7×7×7 k-mesh were used. The magnetic moment of 0.6 (z axis) in order to consider the spin-orbit coupling effect.

The formation energy of Pb or Te vacancy was calculated using Eq. (1)[1]:

$$E_f(\mathrm{V_M}) = E_{tot}(\mathrm{V_M}) + E(\mathrm{M_{bulk}}) - E_{tot} \tag{1}$$

where M represents the Pb or Te atoms, and E_{tot} and E_{tot}(VM) are the total energies of the supercell before and after the introduction of the additional Pb or Te vacancy respectively, $E(\mathrm{M_{bulk}})$ is the energy of a single Pb or Te in its ground state bulk phase. The formation energy of the substitutional Sb in Pb or Te site was calculated using Eq. (2)[2]:

$$E_f(\mathrm{Sb_M}) = E_{tot}(\mathrm{Sb_M}) + E(\mathrm{Sb}) - E_{tot} - E(\mathrm{M}) \tag{2}$$

where M represents the Pb or Te atoms, and E_{tot} and $E_{tot}(\mathrm{Sb_M})$ are the total energies of the supercell before and after the Sb substituting Pb or Te site respectively, E(Sb) and E(M) are the energy of a single Sb atom and Pb or Te atom in its ground state bulk phase, respectively.

Thermal conductivity calculation. Theoretical lattice thermal conductivity, k_L, was calculated by the Boltzmann transport equation basing on the Debye model as shown in Eq. (3):

$$\kappa_L = \frac{\kappa_B}{2\pi^2 v_a}\left(\frac{\kappa_B T}{\hbar}\right)^3 \int_0^{\theta_D/T} \tau_C \frac{e^x}{(e^x-1)^2} x^4 dx \tag{3}$$

Where κ_L is the lattice thermal conductivity, $\hbar$ is the reduced Plank constant, κ_B is the Boltzmann constant, T is absolute temperature, θ_D is the Debye temperature, v_a is an averaged phonon group velocity, x is a dimensionless quantity defined by $x = \hbar\omega/\kappa_B T$ (where ω is the phonon frequency) and τ_c is the combined phonon scattering relaxation time calculated by Callaway model as shown in Eq. (4) to (9)[3, 4]:

$$\tau_C^{-1} = \tau_N^{-1} + \tau_U^{-1} + \tau_{PD}^{-1} \tag{4}$$

where τ_N, τ_U, and τ_{PD} are the relaxation times of Normal scattering, Umklapp scattering and alloying, respectively. Each relaxation time was evaluated as in Eq. (5) - (7).

$$\tau_U^{-1} = \frac{\hbar\gamma^2}{Mv_a^2\theta_D}\omega^2 T exp(-\theta_D/3T) \tag{5}$$

$$\tau_N^{-1} = \beta\tau_U^{-1} \tag{6}$$

$$\tau_{PD}^{-1} = \frac{\omega^4 V_0}{4\pi v_a^3}\Gamma_M \tag{7}$$

Here, γ, M, V_0, β, Γ are the Grüneisen parameter, the average mass of an atom, the volume per atom, the ratio of normal phonon scattering to Umklapp scattering, and the mass-fluctuation phonon scattering parameter, respectively. The relation of the average group velocity v_a, is represented as in Eq. (8), where v_L is the longitudinal sound velocity and v_T is the transversal sound velocity.

$$v_a = \left[\frac{1}{3}\left(\frac{1}{v_L^3} + \frac{2}{v_T^3}\right)\right]^{-\frac{1}{3}} \tag{8}$$

The mass-fluctuation phonon scattering parameter Γ is represented as in Eq. (9), where f_i is the fractional concentration of the atom and M_i is the atomic mass of each atom i.

$$\begin{gathered}\Gamma = \sum_i f_i\left(1 - \frac{M_i}{M_{avg}}\right)^2 \\ M_{avg} = \sum_i f_i M_i\end{gathered} \tag{9}$$

Required parameters are the followings. Phonon group velocities were chosen as 2919 m/s for the longitudinal mode and 1620 m/s for the transverse mode[5], Debye temperature and Grüneisen parameter ware set to be 136 K and 1.96[6]. β was picked as a fitting parameter as chosen as 2.1,

Table S1. Lattice constants, experimental densities, theoretical densities and relative densities for $Pb_{1-x}Sb_xTe$ alloys.

Compositions	**Lattice constants(Å)**	**Experimental Density (g/cm^3)**	**Theoretical Density (g/cm^3)**	**Relative density(%)**
x=0.2%	6.4609	8.040	8.245	98
x=0.5%	6.4616	8.013	8.235	98
x=0.7%	6.4618	7.976	8.230	97
x=1.0%	6.4608	8.108	8.228	98
x=1.2%	6.4591	8.053	8.230	98
x=1.5%	6.4618	7.995	8.213	97

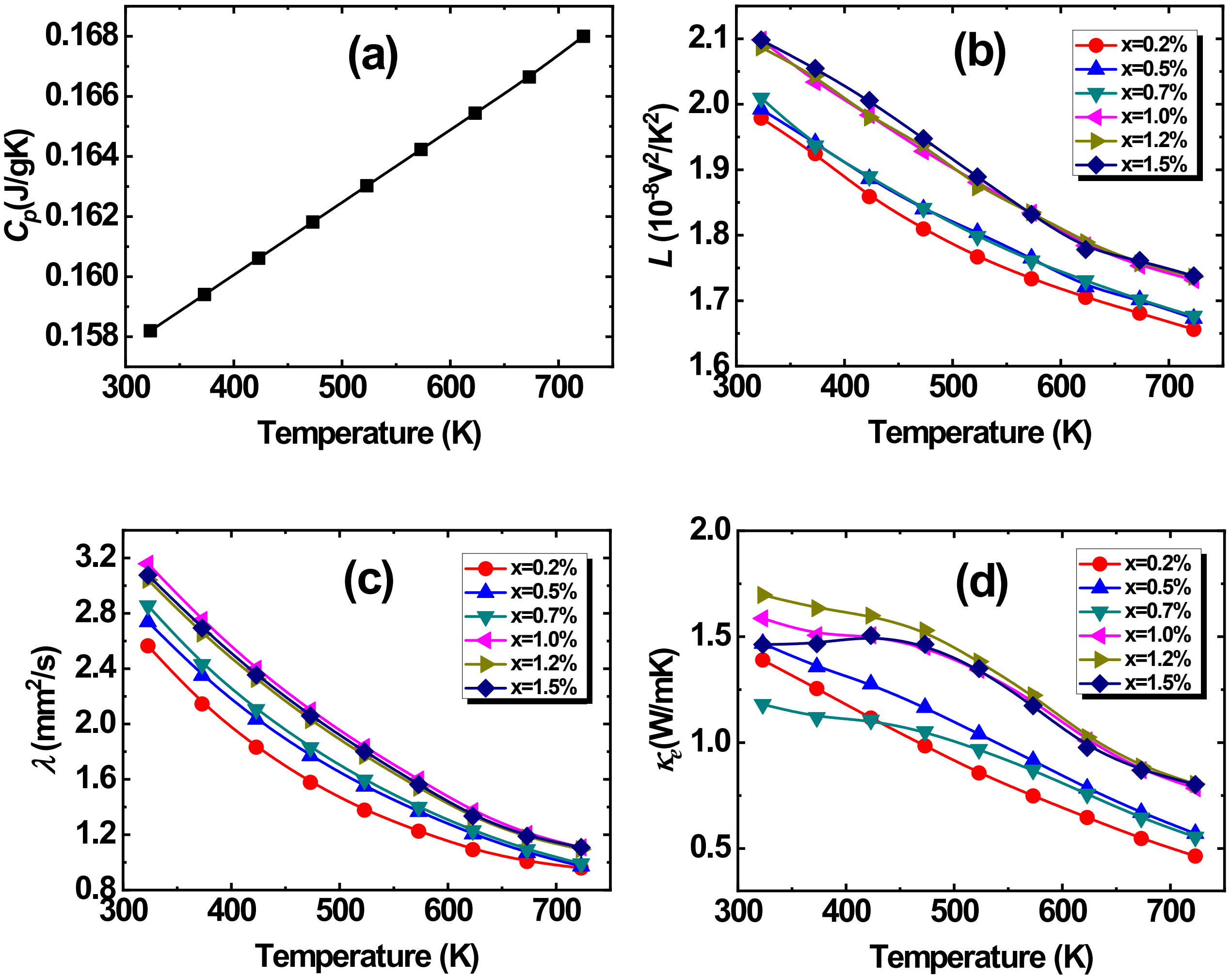

Figure S1 Temperature dependence of **(a)** the heat capacities derived from the equation of *Cp* (k_B atom)=3.07+4.7×10^{-4}×(T/K−300)[7], **(b)** the Lorenz numbers calculated from the equation of L=1.5+exp(-|S|/116)[8], **(c)** the thermal diffusivities, and **(d)** the electronic thermal conductivities for $Pb_{1-x}Sb_xTe$ alloys.

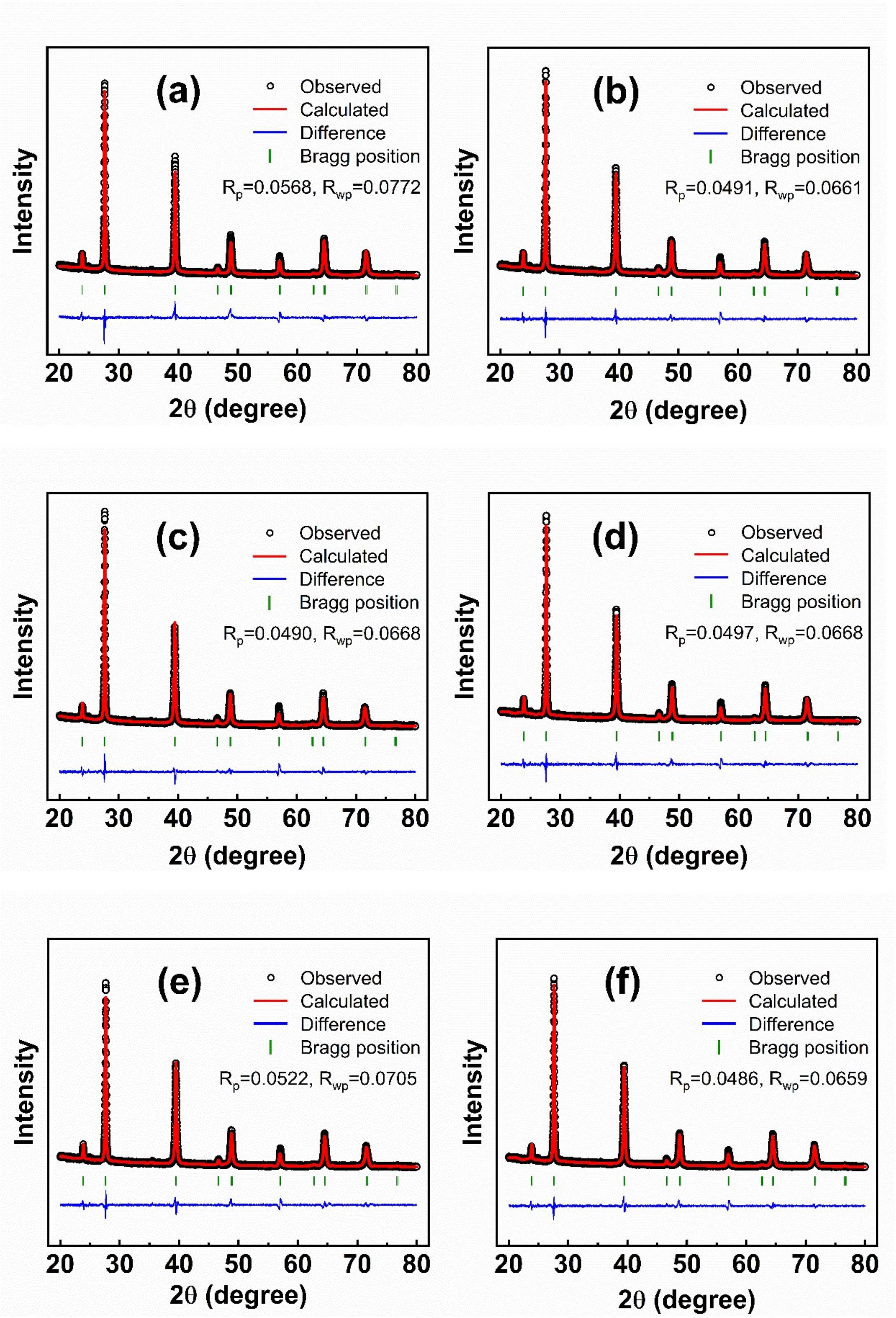

Figure S2 XRD patterns with Rietveld refinement of $Pb_{1-x}Sb_xTe$ bulk alloys for **(a)** x=0.2%, **(b)** x=0.5%, **(c)** x=0.7%, **(d)** x=1.0% **(e)** x=1.2%, and **(f)** x=1.5%.

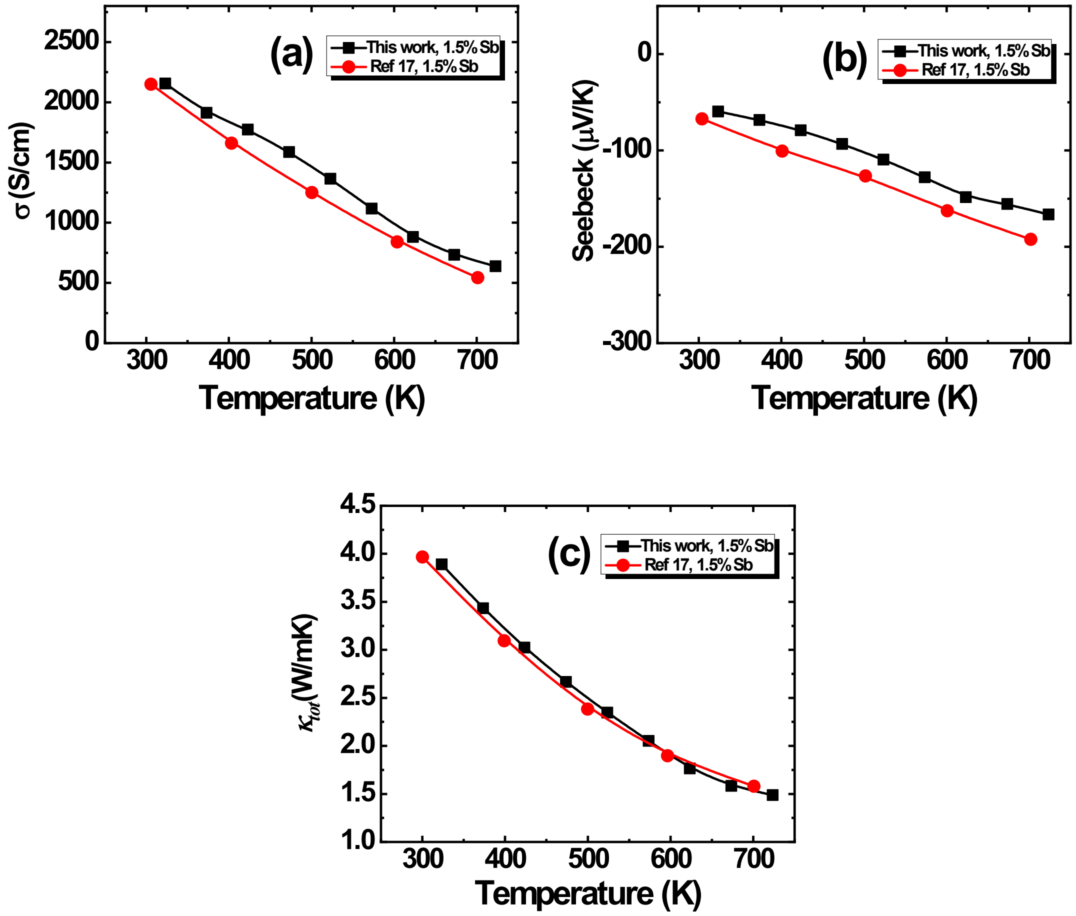

Figure S3 Comparison of **(a)** electrical conductivity, **(b)** Seebeck coefficient and **(c)** thermal conductivity for 1.5% Sb doped PbTe alloys in this work and reported work.

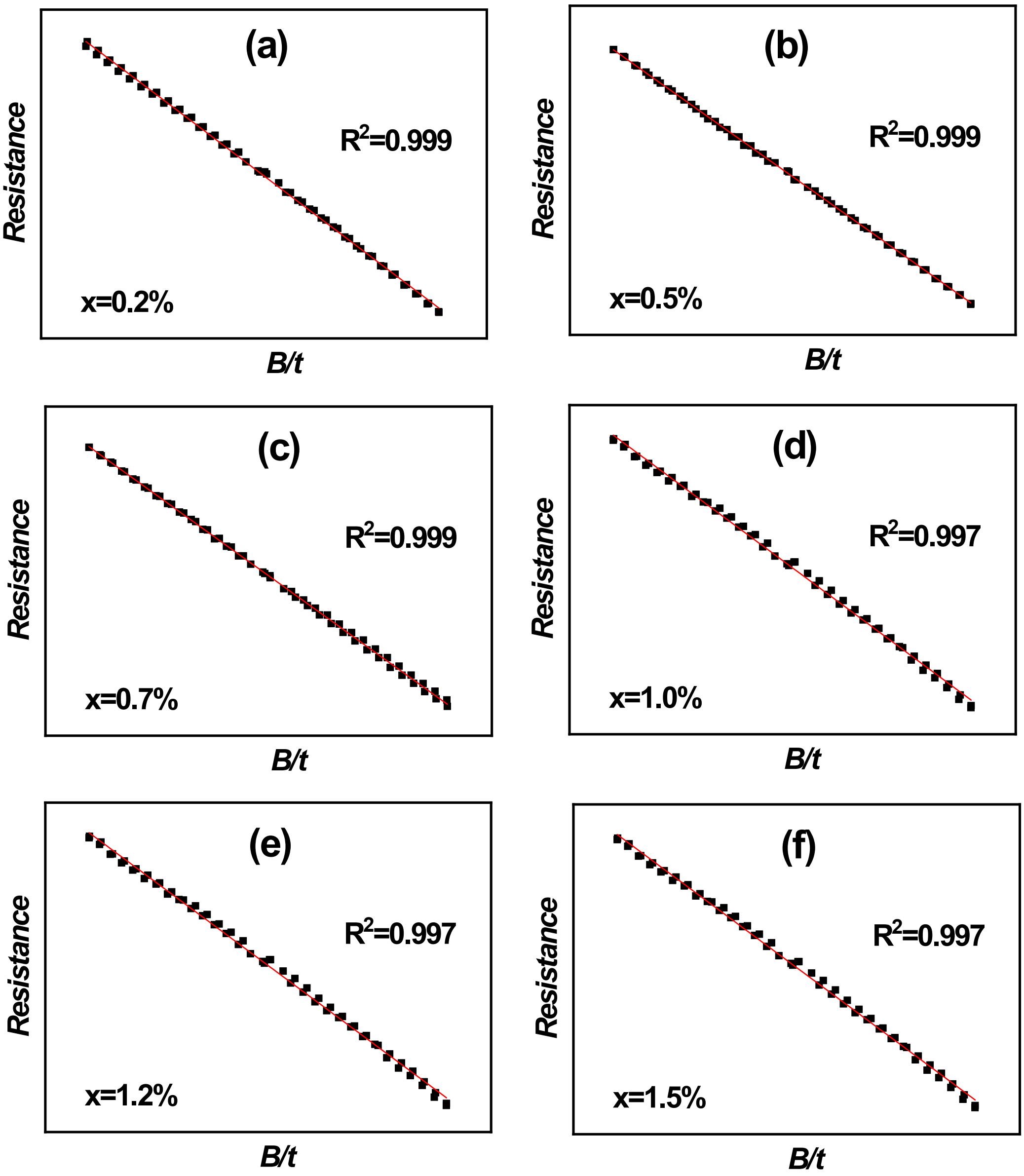

Figure S4 The resistance dependence of the ratio of magnetic field intensity to $Pb_{1-x}Sb_xTe$ samples thickness (*B/t*) for **(a)** x=0.2%, **(b)** x=0.5%, **(c)** x=0.7%, **(d)** x=1.0% **(e)** x=1.2%, and **(f)** x=1.5%. The slope of the resistance versus *B/t* is the Hall coefficient (R_H).

Reference

1. X. Zhang, J. Li, X. Wang, Z. Chen, J. Mao, Y. Chen and Y. Pei, *Journal of the American Chemical Society*, 2018, **140**, 15883-15888.
2. J. Li, X. Zhang, X. Wang, Z. Bu, L. Zheng, B. Zhou, F. Xiong, Y. Chen and Y. Pei, *Journal of the American Chemical Society*, 2018, **140**, 16190-16197.
3. J. Callaway and H. C. von Baeyer, *Physical Review*, 1960, **120**, 1149-1154.
4. B. Abeles, *Physical Review*, 1963, **131**, 1906-1911.
5. L. Fu, M. Yin, D. Wu, W. Li, D. Feng, L. Huang and J. He, *Energy & Environmental Science*, 2017, **10**, 2030-2040.
6. J. He, S. N. Girard, M. G. Kanatzidis and V. P. Dravid, *Advanced Functional Materials*, 2010, **20**, 764-772.
7. R. Blachnik and R. Igel, *Zeitschrift für Naturforschung B*, 1974, **29**, 625–629.
8. H.-S. Kim, Z. M. Gibbs, Y. Tang, H. Wang and G. J. Snyder, *APL Materials*, 2015, **3**, 041506.