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Supporting Information

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High thermoelectric figure of merit and nano-structuring in bulk p-type $Na_{1-x}Pb_mSbTe_{m+2}$

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Materials and methods

Synthesis procedure for $Na_{1-x}Pb_mSb_yTe_{m+2}$.

Polycrystalline ingots of $Na_{1-x}Pb_mSb_yTe_{m+2}$ (where m = 19, 20, 21; $0.80 \leq 1\text{-}x \leq 0.95$; $0.4 \leq y \leq 0.8$) were prepared by reacting Pb (99.99 %), Sb (99.999 %) and Te (99.999 %) with Na (99 %) starting from nominal compositions calculated using the general formula. Pb, Sb and Te elements weighed under ambient atmosphere were first transferred into carbon-coated quartz tubes (Outer diameter = 13 mm, Length ≈ 20 cm) and then placed into a nitrogen-filled glove box to load the alkali metal component. Approximately 20 g of the starting materials were vacuum-sealed in carbon- coated quartz tubes under a residual pressure of $\sim 10^{-4}$ Torr. The sealed tubes were placed into a tube furnace (mounted on a rocking table) and heated up to allow complete melting of all components at 1250 K. While molten the furnace was allowed to rock so to facilitate complete mixing and homogeneity of the liquid phase. After several hours of rocking, the furnace was finally immobilized at ~ 60° tilted position for the crystal growth. The furnace was slowly cooled from 1250 K to 820 K in 43h followed by a fast cool to room temperature. In all cases the resulting product was a lustrous air-stable silver-like polycrystalline ingot (melting point ~1200 K). The elemental compositions reported in this paper are nominal, but they have been confirmed with energy-dispersive spectroscopy analysis. The X-ray powder diffraction patterns (Fig.1) indicated that all $Na_{1-x}Pb_mSb_yTe_{m+2}$ samples prepared in this study appear as single phase with an average NaCl-type structure ($Fm\text{–}3m$). The refined lattice parameter (inset table of Figure 1) remains almost constant (independently of m) around the typical value of 6.461 Å for pure PbTe[1].

Note: the samples obtained from this procedure are often rather brittle. They can contain microcracks which can give lower electrical conductivity values than the intrinsic ones and those reported here.

Thermal Conductivity Measurements. To obtain the thermal conductivity from 300 to 800 K, we measured the thermal diffusivity (α) using the laser flash technique. The thermal conductivity (κ) values were calculated as a product of these quantities, i.e. $\kappa = \alpha C_p d$. where C_p is the specific heat and d is the sample's density. The bulk density (d) values were calculated from the sample's geometry and mass (12 mm in diameter and 2.3 mm thick) and the specific heat (C_p) was measured on a 12 mm in diameter and 1.0 mm thick sample using differential scanning calorimetry.[2]

Thermal diffusivity, Density and Specific Heat data for $\underline{Na_{0.95}Pb_{19}SbTe_{21}}$

Temperature (°C)	Thermal diffusivity (cm^2/s)	Density (g/cm^3)
23.0	0.0135	7.716
50.0	0.0127	7.716
100.0	0.0114	7.716
200.0	0.0091	7.716
300.0	0.0076	7.716
400.0	0.0071	7.716
500.0	0.0073	7.716
525.0	0.0076	7.716

Temperature (°C)	Specific Heat/(J g^{-1}K^{-1})	Temperature (°C)	Specific Heat (J g^{-1}K^{-1})
23.0	0.162	290.0	0.153
50.0	0.162	295.0	0.153
75.0	0.162	300.0	0.152
100.0	0.162	310.0	0.151
125.0	0.162	320.0	0.151
150.0	0.163	330.0	0.152
175.0	0.163	340.0	0.152
200.0	0.163	350.0	0.152
225.0	0.163	360.0	0.152
250.0	0.163	370.0	0.152
255.0	0.159	375.0	0.152
260.0	0.157	400.0	0.152
265.0	0.156	425.0	0.152
270.0	0.155	450.0	0.155
275.0	0.155	475.0	0.159
280.0	0.154	500.0	0.165
285.0	0.154	525.0	0.165

Thermal diffusivity, Density and Specific Heat data for $Na_{0.80}Pb_{20}Sb_{0.6}Te_{22}$

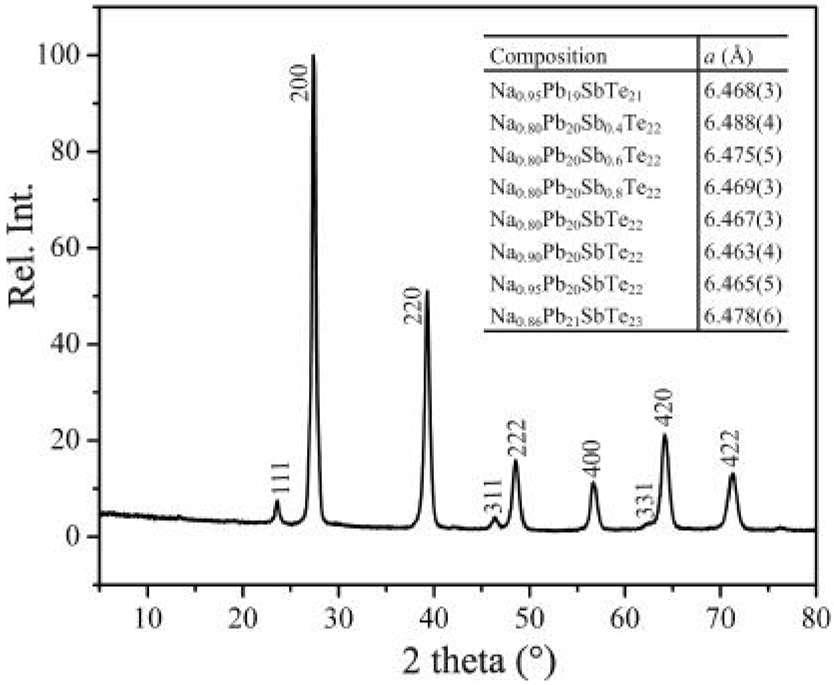
Temperature (ºC)	Thermal diffusivity (cm^2/s)	Density (g/cm^3)
23.0	0.0177	7.795
50.0	0.0161	7.795
100.0	0.0138	7.795
200.0	0.0103	7.795
300.0	0.0076	7.795
400.0	0.0068	7.795
500.0	0.0076	7.795
525.0	0.0080	7.795

Temperature (ºC)	Specific Heat/(J g^{-1}K^{-1})
75	0.161
100	0.161
125	0.161
150	0.161
175	0.161
200	0.161
225	0.162
250	0.162
275	0.162
300	0.162
325	0.161
350	0.161
375	0.161
400	0.161
425	0.161
450	0.160
475	0.158
500	0.158
525	0.161

Thermal diffusivity, Density and Specific Heat data for $Na_{0.95}Pb_{20}SbTe_{22}$

Temperature (°C)	Thermal diffusivity (cm^2/s)	Density (g/cm^3)
23	0.0145	7.875
50	0.0135	7.875
100	0.0117	7.875
200	0.0091	7.875
300	0.0075	7.875
400	0.0067	7.875
500	0.0073	7.875
525	0.0076	7.875

Temperature (°C)	Specific Heat/($J\ g^{-1}K^{-1}$)
75	0.161
100	0.161
125	0.161
150	0.161
175	0.161
200	0.161
225	0.162
250	0.162
275	0.162
300	0.162
325	0.161
350	0.161
375	0.161
400	0.161
425	0.161
450	0.160
475	0.158
500	0.158
525	0.161



Composition	*a* (Å)
$Na_{0.95}Pb_{19}SbTe_{21}$	6.468(3)
$Na_{0.80}Pb_{20}Sb_{0.4}Te_{22}$	6.488(4)
$Na_{0.80}Pb_{20}Sb_{0.6}Te_{22}$	6.475(5)
$Na_{0.80}Pb_{20}Sb_{0.8}Te_{22}$	6.469(3)
$Na_{0.80}Pb_{20}SbTe_{22}$	6.467(3)
$Na_{0.90}Pb_{20}SbTe_{22}$	6.463(4)
$Na_{0.95}Pb_{20}SbTe_{22}$	6.465(5)
$Na_{0.86}Pb_{21}SbTe_{23}$	6.478(6)

Figure 1. A typical X-ray powder diffraction pattern of $Na_{1-x}Pb_mSb_yTe_{m+2}$ samples indicating the cubic $Fm{-}3m$ symmetry. The inset table summarizes the lattice parameter of selected $Na_{1-x}Pb_mSb_yTe_{m+2}$ samples, which were refined from powder data. Diffraction patterns were collected using a Cu Kα (λ = 1.54056 Å) radiation.

High resolution transmission electron microscopy (HRTEM): High resolution transmission electron microscopy images of several pieces cut from different locations of the ingot were recorded at 200 kV using a JEOL JEM 2200FS (Field emission TEM). The images were then analyzed by performing the FFT of different areas using the program ImageJ [W. S. Rasband, ImageJ, U. S. National Institutes of Health, Bethesda, Maryland, USA, http://rsb.info.nih.gov/ij/, 1997-2005.].

Charge Transport Measurements

Rectangular shape samples with typical sizes of 7 mm × 5 mm × 4 mm were employed to simultaneously measure electrical conductivity and thermoelectric power using a four sample measurement system (see Loo, S., Short, J., Hsu, K. F., Kanatzidis, M. G. &

Hogan, *Mat. Res. Soc. Symp. Proc.* 793, 1 (2004)). To fully characterize the figure of merit, the properties were measured for each sample over the selective temperature range of interest. To alleviate offset error voltages and increase the density of data points, a slow-ac technique was used with a heater pulse period of 720 sec. The pulse shape was monitored, in situ, to determine temperature stabilization, and the sample chamber was maintained at a pressure less than 10^{-5} Torr for the entire measurement run. All measurements were performed on a measurement system with capabilities up to 700 K, employing single ended thermocouples for concurrently monitoring the temperature gradient and voltage gradient on the sample.

Sample Preparation for TEM.

The initial starting form of the specimen is typically a section of a cut ingot in the form of a disc approximately one half-inch in diameter, or a rectangular slab a millimeter or more in each dimension. The piece was first attached with low melting point wax (such as Crystalbond 509) to a specimen mount – a cylindrical Pyrex stub 10mm in length and 0.375 inches in diameter. The stub was placed on a hot plate at a temperature of 130°C - 160°C and a small granule of wax is melted on the end of the stub. The specimen section was then placed on the stub and oriented so that two opposite surfaces can be ground flat and parallel to the face of the crystal to be examined. Pre-thinning of the specimen was done with a Gatan Model 623 Disc Grinder (or similar device) to a thickness of 200-400 microns with 600 and 1500 grit silicon carbide paper. A final polish to one or both of the faces was performed with 4000 grit abrasive paper. The polished slab was removed from the mounting stub by melting the wax on a hot place and dissolving the remaining wax in acetone. Once cleaned, the slab was cleaved or cut in rectangular or circular shaped pieces in a size to accommodate the standard 3.01mm TEM specimen holder. Cleaving for rectangular shaped sections was done with a razor blade while circular discs are cut with a Gatan Model 601 Ultrasonic Disc Cutter (an alternative is a South Bay Technology, Inc. Abrasive Slurry Disc Cutter, Model 360 but more time consuming).

Next, a cut section was glued with M-Bond 610 epoxy resin (manufactured by Measurements Group, Inc., Micro-Measurements Division) to a copper aperture grid with a hole size of 1.5/2.0mm, and a diameter of 3.05mm. The adhesive was cured on a hot plate at a temperature of around 160°C for about one-half hour. This composite structure of grid, glue and slab was then attached with low melting point wax to a specimen stub and thinned with a disc grinder to a total thickness of around 140-150 microns. The thickness of the slab at this point is typically about 90–100 microns; the wax, glue, and grid account for about 50 microns. Final polishing was done with 1500 grit silicon carbide paper, and at this stage the sample is ready for dimple grinding.

While still using the Pyrex specimen holder, the sample was placed in the specimen holder of the Gatan Precision Dimple Grinder, Model 656. A 15mm bronze grinding wheel and 6.0 micron diamond paste is used to cut a hemispherical depression (dimple) in the slab to a depth of 40 microns. The initial load on the specimen is 10 grams and the speed is set to 2 (may correlate to 200 RPM). Grinding usually takes from 10 to 20 minutes. The dimple is final polished at slow speed with a felt grinding wheel, 1.0/ 3.0 micron diamond paste, and a load of 3 grams for about 5 minutes. See note below on dimpling.

When the dimpling is complete, the sample is finally ready to be ion milled, after the slab and grid are removed from the specimen stub as described previously. The ion mill is a Gatan Precision Ion Polishing System (PIPS), Model 691. The specimen is mounted on a Gatan DuoPost (a clamp-type holder), the left ion-gun is set at a milling angle of -4°, the right ion-gun is set at a milling angle of +4°, and the beam is configured for dual-beam modulation (polishing is enabled for a sector subtending an angle of 60° between the clamp jaws). Initial beam energy is set to 3.6 keV. Once perforation is detected, the beam energy is reduced to 3.0 keV and milling is continued for about 10 minutes more. Some of the factors affecting the milling time are: the condition of the ion mill (how recently the ion-guns have been cleaned), the volume and shape of the sample, its composition, and its crystallographic orientation. Typical milling times for LAST specimens are from 2 - 4 hours.

Dimpling is crucial for consistent production of these types of PbTe-based samples prepared for TEM. The thickness of the specimen at the center of the slab (location of maximum plasma etching) has to be thin enough so that the time of ion milling is reasonable. Yet, if the whole slab were polished uniformly thick in the range of 70 microns or less, the specimen would be too fragile. By forming a dimple, a thin middle section in the range of 50 - 60 microns thickness is created while the thicker rim (90-100 microns) provides a stronger portion for handling.

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1. Bouad, N., Chapon, L., Marin-Ayral, R.-M., Bouree-Vigneron, F. & Tedenac, J. C. Neutron powder diffraction study of strain and crystallite size in mechanically alloyed PbTe. *J. Solid State Chem.* 173, 189-195 (2003).

2 . The high temperature thermal conductivity measurements for a well grown polycrystalline ingot samples were accomplished by the Thermophysical Properties Research Laboratory Inc., West Lafayette IN 47906, USA (www.tprl.com/).