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Supporting Information

Record figure of merit values of highly stoichiometric Sb_2Te_3 porous bulk synthesized from tailor-made molecular precursors in ionic liquids

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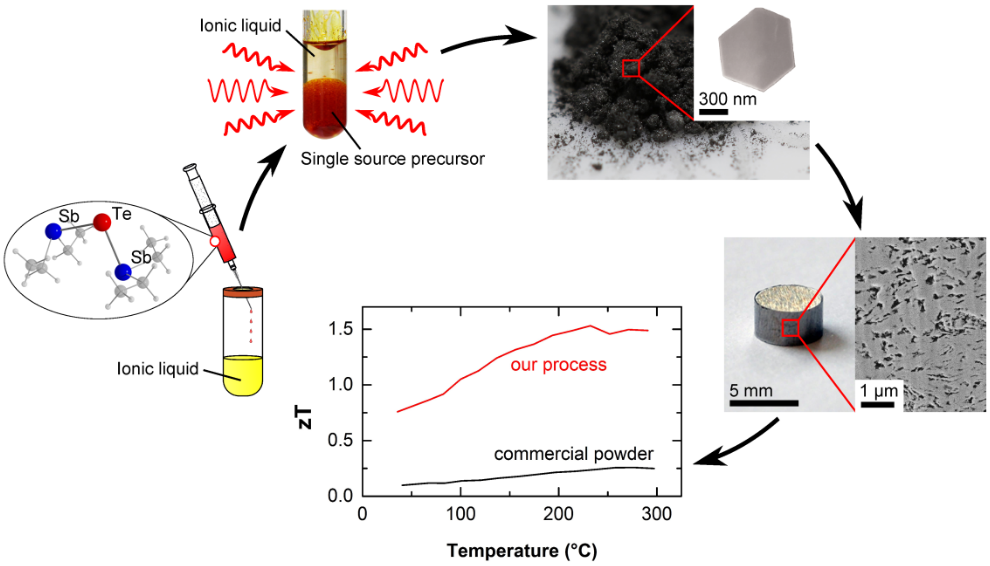

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Experimental Section

A) Precursor Synthesis

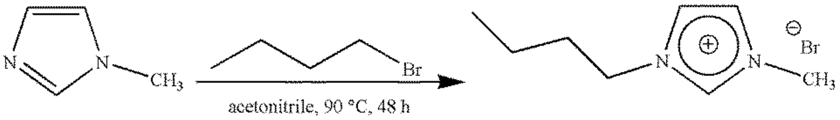
$(Et_2Sb)_2Te$ was synthesized under an Ar atmosphere (using standard Schlenk techniques) by reaction of tetraethyldistibine Et_4Sb_2 with elemental Te in *n*-hexane according to a slightly modified literature method.[1] Yield: 9.29 g (98%). **^{1}H-NMR** (300 MHz, C_6D_6): δ (ppm) 1.31 (t, $^3J_{HH}$ = 7.70 Hz, 12H, CH_3), 1.54 – 1.65 (m, 4H, CH_2), 1.72 – 1.84 (m, 4H, CH_2). **^{13}C-NMR** (75 MHz, C_6D_6): δ (ppm) 8.11 (CH_2), 13.97 (CH_3).

$$Et_4Sb_2 + Te \xrightarrow{25\ ^\circ C} (Et_2Sb)_2Te$$

B) Choice of the IL

Different ionic liquids with various cations (trihexyltetradecylphosphonium, P66614; N-butyl-N-methylpyrrolidinium, C4C1pyr; 1-alkyl-3-methylimidazolium, CxC1im (x=3-8, 12)) and anions (Cl; Br; I; , dicyanamide, DCA; bis(trifluorosyfonyl)amid, NTf_2; tetrafluoroborate, BF_4; hexafluorophosphate, PF_6) were systematically screened. They were chosen to screen over a wide range of sizes and ion potential, Lewis acidity and basicity as well as coordination modes. The trishexyltetradecylphosphonium cation a features long saturated alkyl chains and is known to render an ionic liquid hydrophobic and extremely weakly coordinating, N-butyl-N-methylpyrrolidinium, is a smaller saturated quaternary ammonium cation (thus the charge concentration on the cation is higher and the cation can interact more strongly). N-alkyl-3-methylimidazolium cations with alkyl chain lengths ranging from three to eight and twelve carbon atoms were investigated as imidazolium cations are one of the most commonly applied IL cations which reliably lead to the formation of a low melting salt. The imidazolium group can interact via its aromatic p system and through the fairly acidic ring hydrogen atoms. By extending the carbon chain length it is possible to lower the charge concentration which reduces electrostatic interactions, at the same time van-der-Waals interactions become more important [2]. Albeit we found that the influence of the anion on nanoparticle formation in ionic liquids is less pronounced, their influence is not negligible [3]. For that reason we have investigated anions with different Lewis basicity [4]: chloride, bromide, iodide, dicyanamide, bis(trifluoromethanesulfonyl)amide, tetrafluoroborate and hexafluorophosphate.) In addition, the respective cation-anion combination of the ionic liquid also determines the melting point and viscosity which are important parameters in the synthesis. To prove the benefit of the microwave-assisted decomposition of the single-source precursor we carried out classical thermal decomposition experiments. In summary, $[C_4mim]Br$ (C_4mim = 1-butyl-3-methylimidzolium) as the ionic liquid combined with microwave heating proved to give the best results for the production of phase pure Sb_2Te_3 nanoparticle-agglomerates of high performance as a thermoelectric material. IR and EDX proved that the particle surface was free from any organic contaminations.

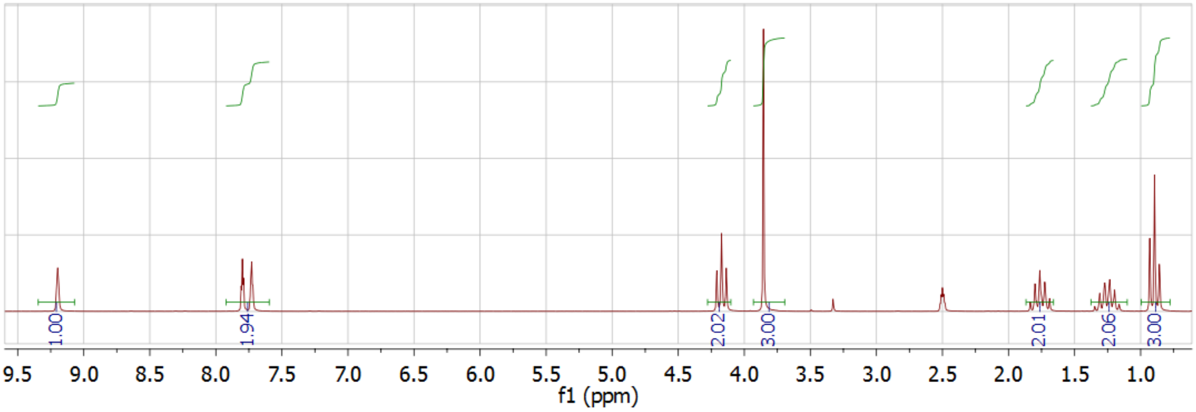
Synthesis of 1-Butyl-3-methyl-imidazolium bromide (C$_4$mimBr)



Supplementary Scheme S1. Synthesis of 1-Butyl-3-methyl-imidazolium bromide.

1-Methylimidazole (23 mL, 0.289 mol; 99%, Sigma Aldrich) and 1-bromobutane (46.4 mL (0.434 mol; 99%, Acros) were heated in 250 mL acetonitrile (99.9+%, Extra Dry, Acros organics) under reflux at 90 °C for 48 h. After cooling to ambient temperature, the solvent was removed under vacuum. The resulting viscous oil was added dropwise under constant stirring to ethyl acetate at 0 °C. After the solvent was removed the white residue was dried from any remaining solvent for 72 h under dynamic vacuum at 50 °C. Yield: 60 g (94%).

^{1}H-NMR (200 MHz, DMSO-d$_6$): δ (ppm) 9.20 (s, 1H), 7.76 (d, J = 14.0 Hz, 2H), 4.17 (s, 2H), 3.86 (s, 3H), 1.77 (s, 2H), 1.24 (s, 2H), 0.90 (s, 3H).



Supplementary Figure S1. ^{1}H-NMR of C$_4$mimBr in DMSO-d$_6$

C) Thermal decomposition of bis(diethylstibino)telluride ($(Et_2Sb)_2Te$) in C_4mimBr

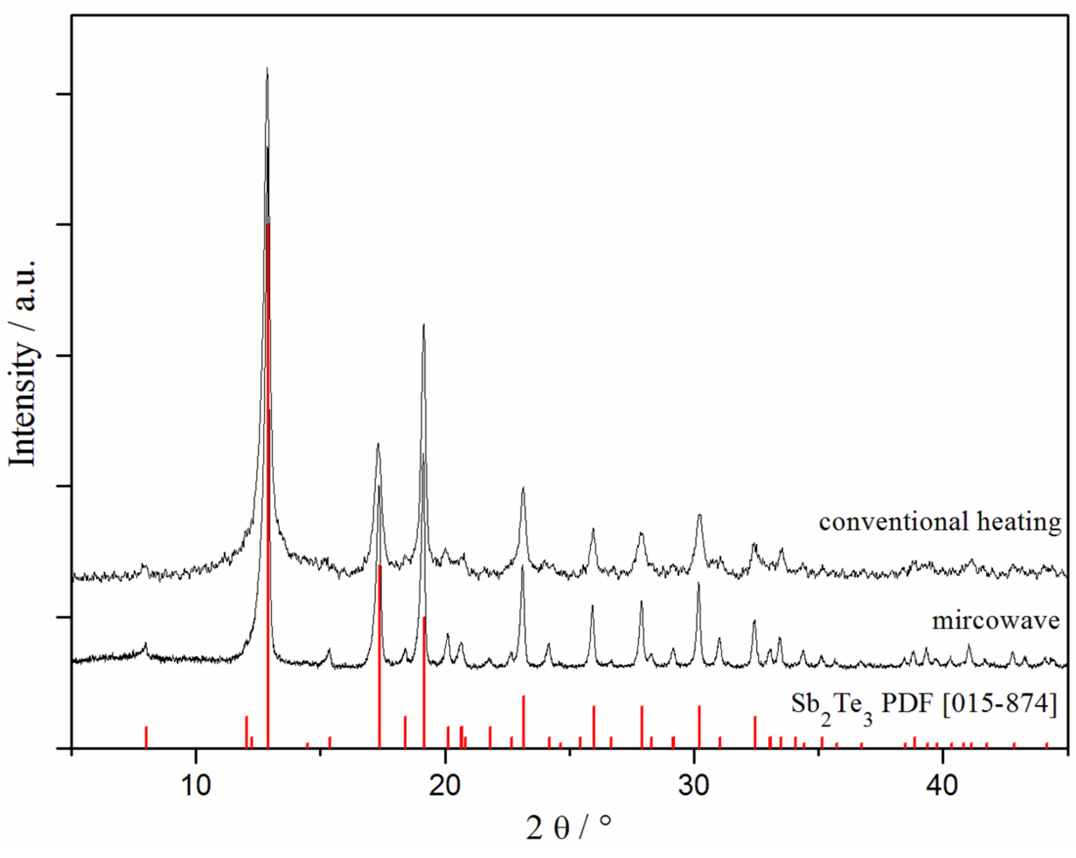
All synthetic steps were performed under inert conditions (Ar atmosphere) in a glovebox or using standard Schlenk techniques.

A) Microwave Synthesis

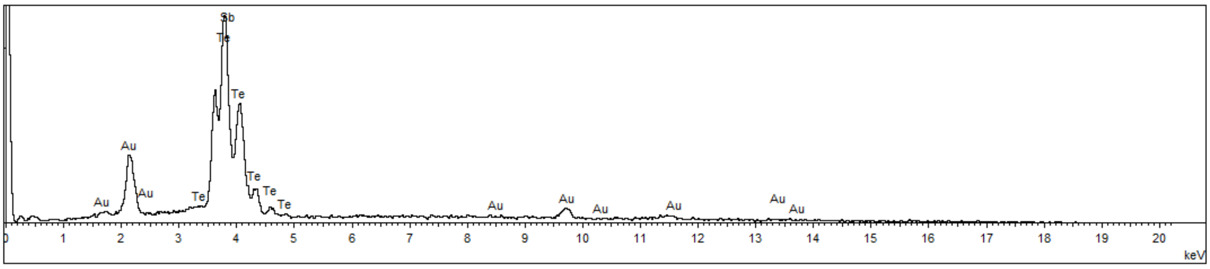
1.18 g (2.42 mmol) of $(Et_2Sb)_2Te$ were added to 3 g (13.7 mmol) molten (90 °C) C_4mimBr and stirred for 5 min. The resulting homogeneous dispersion was heated in a laboratory microwave (Discover, CEM) for 30 s at 100 °C, subsequently for 5 s at 150 °C and finally for 5 min at 170 °C. The obtained colloidal solution was centrifuged (2000 rpm), washed with 7 x 10 mL acetonitrile and dried at room temperature under vacuum.

B) Conventional Heating Synthesis

1.18 g (2.42 mmol) of $(Et_2Sb)_2Te$ were added to 3 g (13.7 mmol) molten (90 °C) C_4mimBr and stirred for 5 min. The resulting homogeneous dispersion was heated in an oil-bath for 4 h at 170 °C, yielding a colloidal solution that was centrifuged (2000 rpm), washed with acetonitrile (7 x 10 mL) and dried at ambient temperature under vacuum.



Supplementary Figure S2. Powder X-ray diffraction pattern of Sb_2Te_3 particles as-synthesized in C_4mimBr using either microwave irradiation or conventional heating.



Supplementary Figure S3. EDX spectrum of Sb_2Te_3 powder synthesis by microwave. Coated with gold on a carbonwaver

D) Material characterization

The resulting Sb_2Te_3 powders were characterized by powder X-ray diffraction (PXRD, Huber 670, Molybdenum Mo K_α radiation (0.0709 nm). PXRD patterns from Sb_2Te_3 pellets were obtained using a Bruker D8 Advance powder diffractometer using Cu K_α radiation. Particle size and morphology were analyzed by scanning electron microscopy (SEM) using a Jeol JSM 6510 microscope. For SEM analysis, the samples were coated with a thin gold layer. The elemental composition of the material was analyzed by energy-dispersive X-ray analysis (EDX) using a Bruker Quantax 400 spectrometer.

E) Powder Compaction

The nanocrystalline Sb_2Te_3 powder was cold pressed applying a pressure of 815MPa for 30 min using a pressing tool with 5 mm in diameter. After pressing, the samples were annealed for one hour at 300 °C in vacuum at $1*10^{-6}$ mbar. The geometric density of the resulting pellets was found to range from 75 to 90 %.

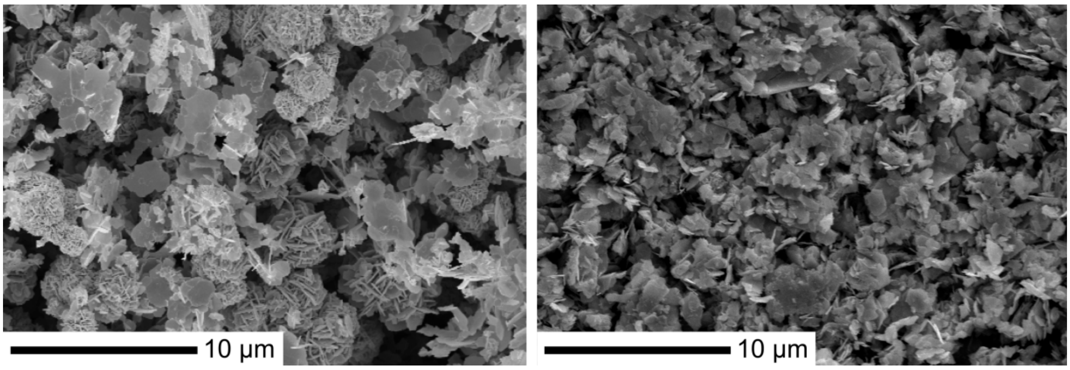
F) Thermoelectric characterization

The Seebeck coefficient α and the electrical conductivity σ were measured by a direct measuring technique using the commercial system ZEM-3 from Ulvac Technologies, Inc., from room temperature up to 300 °C. Thermal diffusivity was measured by a Laserflash System LFA 457 (Netzsch) from the same sample after characterization of the electronic transport properties. To calculate the thermal conductivity κ from the diffusivity, the literature value of heat capacity according to [5] was used. All measurements were done in the cross plane (z-) direction analogous to the pressing direction.

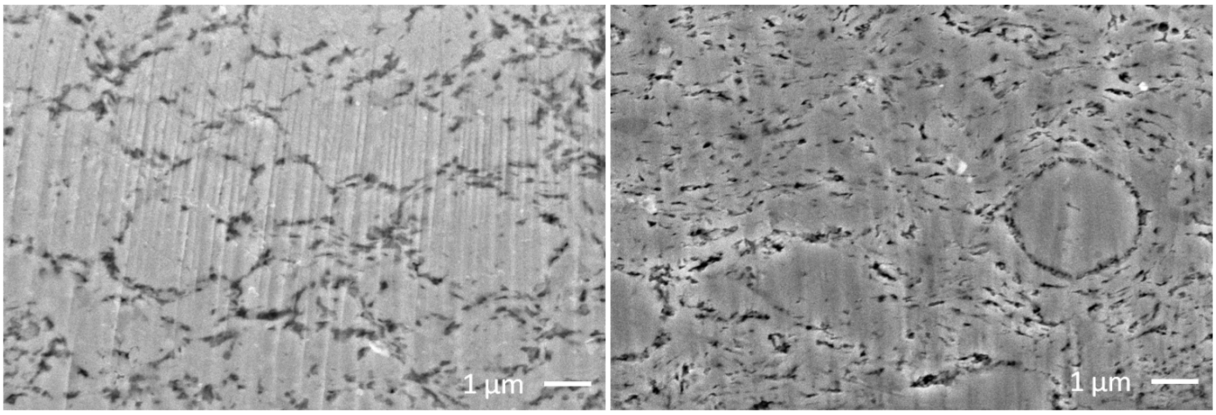
Hall measurements were performed on all samples in van-der-Pauw geometry using a Physical Property Measurement System (PPMS) by Quantum Design, Inc. Measurement were done on the same but considerably thinned pellets as used for the thermal conductivity measurements, hence along the transport direction perpendicular to the pressing direction. These measurements were used to calculate the charge carrier density n which is assumed to be isotropic. The mobility μ was derived from the conductivity measurement described above according to $\sigma = n\ e\ \mu$.

G) Characterization of compacted Sb_2Te_3 pellets

Cross section samples of the Sb_2Te_3 pellets were prepared by use of a Jeol Cross Section Polisher (IB-09010CP) and analyzed using a Jeol JSM 6510 microscope (SEM, morphology) equipped with a Bruker Quantax 400 spectrometer (EDX, chemical composition).



Supplementary Figure S4: SEM images of particles processed within 5 min in the microwave and 4 hours in an oil bath.



Supplementary FigureS5: SEM images of the cross-sectional area of the pellets processed in the microwave (left) and in an oil bath (right).

References

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