Energy Materials

Supplementary Material

Scalable solution chemical synthesis and comprehensive analysis of Bi_2Te_3 and Sb_2Te_3

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Supplementary Table 1. Literature review on microwave (MW) assisted synthesis of binary phases of Bi_2Te_3 and Sb_2Te_3; Details of the synthetic route, solvent, reaction temperature-time; morphology of resultant structures; the quantity typically obtained according to described procedure in the articles, and the reported transport data.

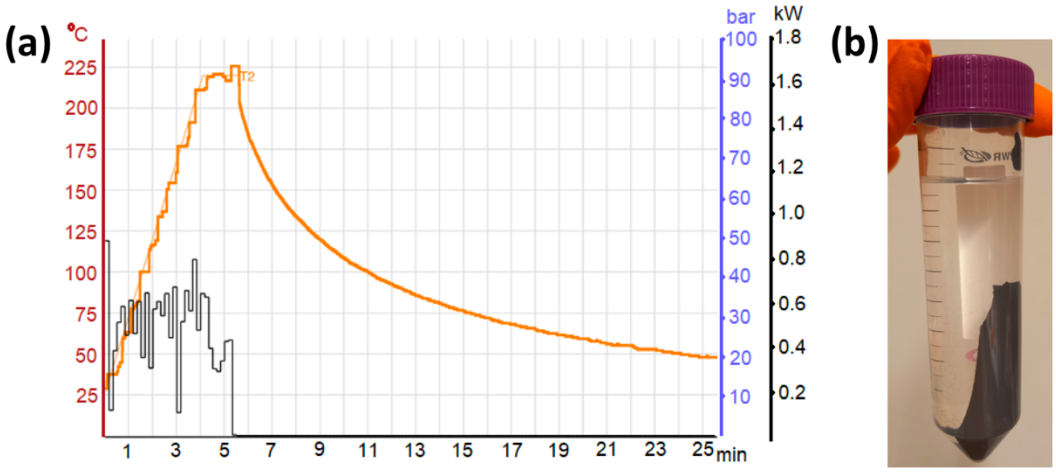
Composition	Synthetic route, Solvent	Rxn T and time	Morphology; Quantity*	*ZT*	Ref
Bi_2Te_3	MW, polyol (EG); reflux system	T: No data t: 0.5–6 h	Nanorod; 1 mmol; 0.8 g	No data	[1]
Bi_2Te_3	MW, mixed solvents of water and ethylene glycol (EG)	T: 150 °C t: 30 min	Hollow spheres 0.2 mmol; 0.16 g	No data	[2]
Bi_2Te_3	MW, mixed solvents of water, and ethylene glycol (EG)	T: 150 °C t: 30 min	Hollow spheres, nanosaws, sheets; 0.03 mmol; 0.025 g	No data	[3]
Bi_2Te_3	MW, polyol (EG)	T: 170–195 °C t: 30–60 min	Nanosheets and nanotubes 0.13 mmol; 0.11 g (based on Te)	No data	[4]
Bi_2Te_3	MW; reduction in water; reflux system	T: No data t: 10 min	Nanocrystals; 1 mmol; 0.8 g	***ZT***: 1.18 @300 K	[5]
Bi_2Te_3	MW, polyol (EG)	T: 220 °C t: 2 min	Hexagonal platelets; 8 g	***ZT***: **1.04** @440 K	[6]ϒ
Sb_2Te_3	MW, polyol (EG)	T: 220 °C t: 2 min	Hexagonal platelets; 8 g	***ZT***: **1.37** @523 K	[6]ϒ
Bi_2Te_3	MW, Hydrothermal	T: 220 °C t: 2 min	Hexagonal platelets; 8 g	***ZT***: **0.9** @373 K	[7]ϒ
Sb_2Te_3	MW, Hydrothermal	T: 220 °C t: 2 min	Hexagonal platelets;	***ZT***: **1.03** @473 K	[7]ϒ

			8 g		
Bi_2Te_3	MW, thermolysis	T: 220 ◦C t: 2 min	Hexagonal platelets; 16 g	***ZT***: **0.7** at 573 K	This work
Sb_2Te_3	MW, thermolysis	T: 220 ◦C t: 2 min	Hexagonal platelets; 16 g	***ZT***: **0.9** at 523 K	This work

*Quantity is estimated from the experimental details given in the respective articles, assuming 100% yield.

ϒThese are our earlier works on MW-assisted polyol and hydrothermal routes.

A typical reaction profile in the MW-reactor is displayed in **Supplementary Figure 1a,** where the ramping time (4 min), dwell time (2 min) and consumed MW power can be clearly seen. The products are also easily separable from the reaction mixture, as displayed in **Supplementary Figure 1b.**



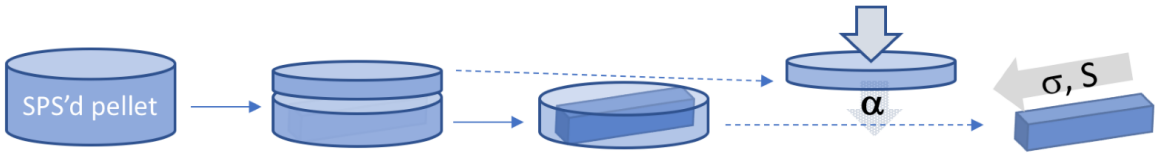
Supplementary Figure 1. (a) MW-assisted reaction profile used for the synthesis of Bi_2Te_3 and Sb_2Te_3 nanoparticles. (b) Picture showing the quantity of materials obtained in a single reactor, and easy separation of particles from the reaction mixture.

MW-assisted heating provides uniform heating throughout the reaction mixture, which ensures consistent conditions and reduces temperature gradients. This method also allows for rapid heating and cooling, giving precise control over reaction times and temperatures, with drastically reduced reaction time as compared to conventional synthetic routes. The precision of the MW system helps to achieve consistent particle size, crystallinity and morphologies across different batches. Additionally, it's scalable, meaning it can be used for both small and large batches without significant changes in reaction conditions, ensuring the same quality of nanoparticles regardless of batch size. The method also allows for better control over the reaction environment, including atmosphere and pressure, essential for maintaining consistent conditions, significantly reducing time and energy consumption. With the FlexiWAVE MW system, with its 15 (each 100ml) vials (see **Supplementary Figure 2**), we can produce large quantities of materials in one run. Samples in multiple vessels were characterized with X-ray diffraction (XRD) and establish the phase purity, before mixing to ensure the scale-up reproducibility of the TE materials.

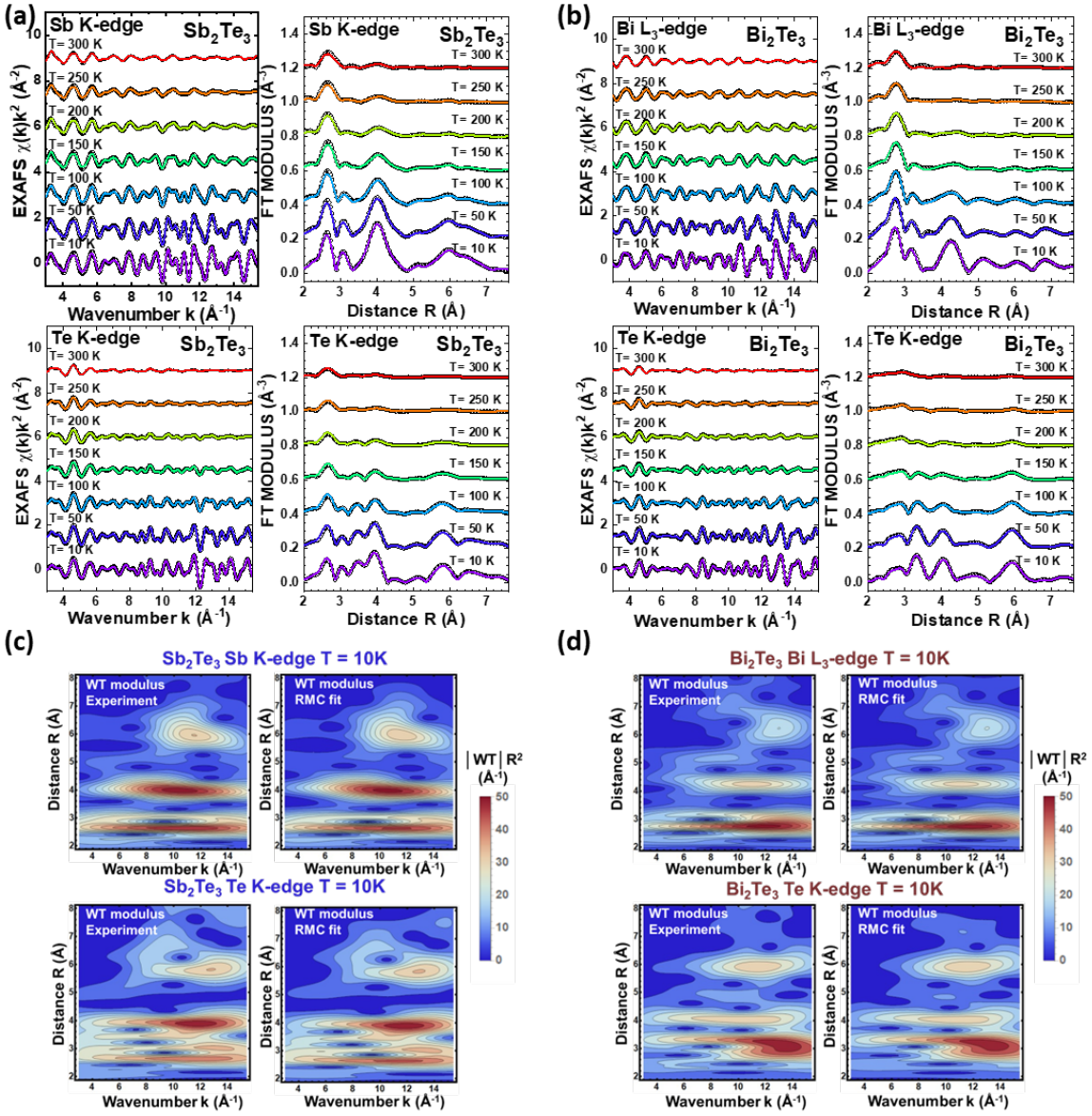
(a) (b)

Supplementary Figure 2. (a) Screenshot of the MW reactor, for experimental design, with multivessel rotor; (b) Multivessel high pressure rotor used for the MW assisted synthesis of Bi_2Te_3 and Sb_2Te_3 nanoparticles. The system can take up to 15 reactors which can be filled up to about 100 mL each, making it possible to synthesize high and reproducible quality nanostructures with a high yield, at a pilot scale, without needing any complicated or reflux systems.

The thermal conductivity is estimated through thermal diffusivity ($\boldsymbol{\alpha}$) measurements using a thin (2 mm thick) disk-shaped sample, cut from the SPS compacted pellet (see **Supplementary Figure 3**). The $\boldsymbol{\alpha}$ measurement direction is parallel (cross-plane) to the pressing direction. Other electronic properties, $\boldsymbol{S}$ and electrical conductivity ($\boldsymbol{\sigma}$), are measured in perpendicular plane to the pressing direction (in-plane). This is a common practice in the transport property evaluation of bulk TE materials.



Supplementary Figure 3. Sample geometry and measurement direction of electronic and thermal transport properties ($\boldsymbol{\alpha}$: Thermal diffusivity, $\boldsymbol{\sigma}$: Electrical conductivity; $\boldsymbol{S}$: Seebeck coefficient).



Supplementary Figure 4. A comparison of the experimental and RMC/EA calculated Sb K-edge and Te K-edge EXAFS spectra $\chi(k)k^2$ and their moduli of their Fourier and Morlet wavelet transforms for the Sb and Te K-edges in Sb_2Te_3 (a,c) and Bi L_3-edge and Te K-edge in Bi_2Te_3 (b,d). Wavelet transforms, representing data in k and R space simultaneously, are shown for data corresponding to 10 K only.

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