Chemical Routes to Nanocrystalline Thermoelectrically Relevant $AgPb_mSbTe_{m+2}$ Materials

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Supplementary information

Typical Procedure for the synthesis of nanoparticles

Reverse micellar solutions of sodium dodecyl sulfate (SDS) were prepared in a sealed vial as described elsewhere. An amount of 3g SDS was mixed with 11g of octane and 2.5g of 1-butanol to form a milky solution. An amount of 1.5 gm of water was then added to the milky solution to form a clear solution upon stirring. The solution was allowed to stir for 1 h and then allowed to stand for 2 h. No turbidity or settling was observed over this period.

Five such reverse micellar solutions were prepared and in each one $AgNO_3$, potassium antimony tartrate, $Pb(NO_3)_2$, Na_2TeO_3/ K_2Te and $NaBH_4$ salts were added respectively. $AgNO_3$ solutions were kept in a dark vial to prevent reduction to metallic Ag. The molar quantities of all the emulsions were in the range 0.1-0.6 and are summarized in the supplementary material. The emulsions/solutions of Ag, Sb and Pb were mixed and allowed to stir for 1 h. The emulsion containing the Te precursor (K_2Te for m=0 and Na_2TeO_3 for m=1 and m=2) was then added to the mixture to form a translucent emulsion. Stirring continued for 2-3 h and to it the micro-emulsion containing $NaBH_4$ was then added at once. The color changed instantaneously from translucent milky to black, and the reaction continued for 5-6 h to ensure complete reduction. The reaction mixture was then allowed to stand until the octane evaporated completely thereby leaving a white surfactant mass containing black particles. The excess surfactant was washed off with copious ethanol to yield the black particles.

Table 1: The constituents of microemulsions used in the synthesis of $AgSbTe_2$

	Microemulsion 1 ($AgNO_3$)	Microemulsion 2 $K_2(SbC_4H_2O_6)_2.3H_2O$	Microemulsion 3 (K_2Te)
SDS	3.0 g	3.0 g	3.0 g
Octane	11.0 g	11.0 g	11.0 g
1-butanol	2.5 g	2.5 g	2.5 g
Water	1.5 g	1.5 g	1.5 g
mM (mmol for each reagent)	0.30	0.15[(a)]	0.6

(a) Notice the 0.15 mM $K_2(SbC_4H_2O_6)_2.3H_2O$ corresponds to two equivalents of Sb. This ensures that the metal ratio of Ag/Sb/Te is 1/1/2.

Table 2: The constituents of microemulsions used in the synthesis of $AgPbSbTe_3$

	Microemulsion 1 ($AgNO_3$)	Microemulsion 2 ($Pb(NO_3)_2$	Microemulsion 3 $K_2(SbC_4H_2O_6)_2.3H_2O$)	Microemulsion 4 (Na_2TeO_3)
SDS	3.0 g	3.0 g	3.0 g	3.0 g
Octane	11.0 g	11.0 g	11.0 g	11.0 g
1-butanol	2.5 g	2.5 g	2.5 g	2.5 g
Water	1.5 g	1.5 g	1.5 g	1.5 g
mM (mmol for each reagent)	0.3	0.3	0.15	0.9

(a) Notice the 0.15 mM $K_2(SbC_4H_2O_6)_2.3H_2O$ corresponds to two equivalents of Sb. This ensures that the metal ratio of Ag/Pb/Sb/Te is 1/1/1/3.

Table 3: The constituents of microemulsions used in the synthesis of $AgPb_2SbTe_4$.

	Microemulsion 1 ($AgNO_3$)	Microemulsion 2 ($Pb(NO_3)_2$	Microemulsion 3 ($K_2(SbC_4H_2O_6)_2.3H_2O$)	Microemulsion 4 (Na_2TeO_3)
SDS	3.0 g	3.0 g	3.0 g	6.0 g
Octane	11.0 g	11.0 g	11.0 g	22.0 g
1-butanol	2.5 g	2.5 g	2.5 g	5.0 g
Water	1.5 g	1.5 g	1.5 g	3.0 g
mM (mmol for each reagent)	0.3	0.6	0.15	1.2

Note: It is extremely important to control the concentrations of the ingredients in the emulsion. Deviations from concentration, primarily due to evaporation of octane, resulted in poor quality nanoparticles with aggregation. Repeated attempts to synthesize $AgSbTe_2$ using Na_2TeO_3 and a co-reduction approach did not yield a phase pure material always showing the presence of Sb_2Te_3. The presence of the latter was minimized only when K_2Te was used.

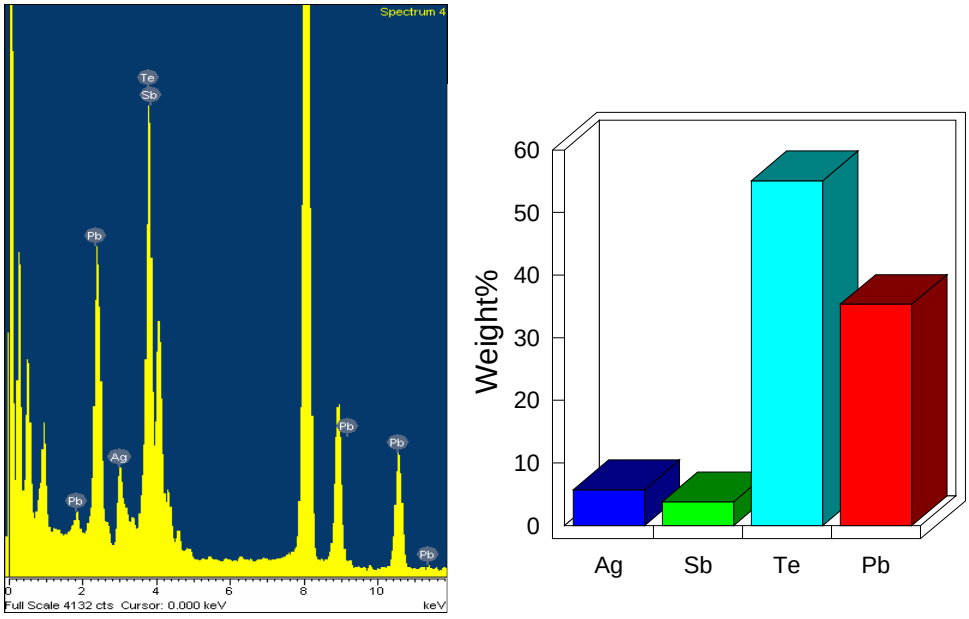
PbTe: The same procedure used to produce the quaternary phase if repeated without $AgNO_3$ and ($K_2(SbC_4H_2O_6)_2.3H_2O$) yield nanoparticles of PbTe ($m=\infty$).

The products must be washed repeatedly with ethanol and water to remove any soluble impurities.

EDS data for $AgPb_2SbTe_4$ *m*=2 measured on a JEOL 2200 FS Transmission electron microscope.

a) Spectrum showing the elements present in the nanoparticles analyzed.

b) Table showing qualitatively the elements found in a single nanoparticle. (***caution*:** this table is only qualitative in nature. Accurate quantitative EDS elemental analysis conducted on individual particles using the JEOL 2200 FS Transmission electron microscope cannot be obtained due to uncertainties in sample thickness and density). That all elements expected to be present in a nanocrystal of $AgPb_2SbTe_4$ are indeed observed, coupled with the smaller lattice parameter observed (than PbTe (6.45(1) Å vs 6.55(1) Å)) supports the view that the nanocrystals are single phase and not a phase separated collection of PbTe and $AgSbTe_2$ or PbTe and Te.



Quantitative microprobe analyses were performed on a JEOL JSM-6400V scanning electron microscope (SEM) equipped with a Noran energy dispersive spectroscopy (EDS) detector. Data acquisition was performed with an accelerating voltage of 20 kV and 60 s accumulation time. These results (which average over several nanoparticles) were consistent with the formula $AgPb_2SbTe_4$ (See Table 1 of article).

Diffuse reflectance UV/Vis/Near-IR Spectroscopy. Optical diffuse reflectance measurements were performed at room temperature using a Shimadzu UV-3101PC double-beam spectrophotometer. The instrument is equipped with an integrating sphere and controlled by a personal computer. $BaSO_4$ was used as a 100% reflectance standard.

The sample was prepared by spreading the nanocrystals on a compacted surface of the powdered standard material, preloaded into a sample holder. The reflectance versus wavelength data generated was used to estimate the band gap of the material by converting reflectance to absorption data using Kubelka-Munk function as described in the reference[1].

[1] (a) Aitken, J. A.; Marking, G. A.; Evain, M.; Iordanidis, L.; Kanatzidis, M. G. *J. Solid State Chem.* **2000**, *153*, 158. (b) Kortèum, G. *Reflectance spectroscopy. Principles, methods, applications*; Springer: Berlin, Heidelberg, New York, 1969.