

Electronic Supplementary Information

Rapid Direct Conversion of Cu_{2-x}Se to CuAgSe Nanoplatelets via Ions Exchange Reactions at Room Temperature

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Experimental details

Nanoplatelets of copper selenide, Cu_{2-x}Se , were formed using a solvothermal method first described by D. Chen et al.¹ Copper acetate (98%, Sigma Aldrich) and sodium selenite (99%, Sigma Aldrich) were added to 0.2 g of sodium hydroxide ($\geq 97\%$, Sigma Aldrich), 10 ml of ethylene glycol (Sigma Aldrich), and 20 ml of distilled water in Teflon liners. Stoichiometric ratios of copper acetate to sodium selenite reflecting the Cu_2Se and CuSe_2 products were used in the mixture: 0.18 g of copper acetate and 0.35 g of sodium selenite for Cu_2Se , and 0.09 g of copper acetate and 0.035 g of sodium selenite for CuSe_2 . The mixture was stirred in the Teflon liners for 30 minutes and filled to 75% of the volume of the each liner. 2 ml of hydrazine hydrate (80%) (Sigma Aldrich) was added to the mixture and stirred for an additional 15 minutes, turning the mixture black and precipitating the solids. The Teflon liners were then placed in stainless steel bombs and heated in a furnace at 140 °C for 12 hours with a ramp up rate of 10 °C/min. The bombs were then cooled at an approximate rate of 25 °C/hr. The contents of the Teflon liners were then centrifuged at 3,000 RPM for 5 minutes and washed with ethanol. The contents were washed a minimum of three repetitions and then dried in a drying oven at 60 °C.

CuAgSe nanoplatelets were formed by partial replacement of copper cations in Cu_{2-x}Se nanoplatelets through an ion exchange reaction similar to the technique utilized by C. Nethravathi et al.² Silver nitrate (Sigma Aldrich) were added to ethanol in a glass vial and sonicated for up to 1 hour for complete dissolution. Dried copper selenide nanoplatelets were then added to the AgNO_3 solution and sonicated for 1 hour at room temperature. The blue solution containing Cu^+ was decanted and the remaining nanoparticles were washed several times using ethanol. The product is then dried in a drying oven at 60 °C until all of the ethanol has evaporated. The converted CuAgSe nanoplatelets were then collected in glass vials for further characterization.

Dense pellets of the mixed-polymorph CuAgSe material were produced by placing ~1 g of material in a graphite die with a diameter of 10 mm. The die was then placed in a GT Advanced Technologies vacuum uniaxial hot press. Pellets were pressed at 100 MPa under vacuum at three temperature histories: 1) at 150 °C for 1 hour with a ramp up and down rate of 75 °C/min, 2) at 450 °C for 1 hour with a ramp up and down rate of 225 °C/min, and 3) at 450 °C for 2 hour with a ramp up and down rate of 225 °C/min. The nanoplatelets for the third pellet were annealed at 450 °C for 1 hour prior to pressing. The densification of the pellets was determined by both the geometric density (measured

volume/measured mass) and the “true” density obtained using by He gas pycnometry using Quantachrome Micro Ultrapyc 1200e.

Phase analysis, crystal structure, and reaction completion were assessed by powder X-ray diffraction techniques using a Rigaku Miniflex 600 with graphite monochromator operating Cu-K α ($\lambda = 1.54056 \text{ \AA}$) at 40 kV and 15 mA, and a Rigaku Ultima with rotating arm anode with graphite monochromator operating Cu-K α ($\lambda = 1.54056 \text{ \AA}$) at 40 kV and 100 mA. Samples of nanoplatelets were placed into a zero-background (silicon) slide with 10 mm diameter window for X-ray powder diffraction. The resulting X-ray powder patterns were analyzed using the Rietveld refinement FullProf software.³ The XRD results of the products of the ion exchange reactions with reactant molar ratios of Ag:Se varying from 0.58 to 0.83 are shown in Figure 1S. Differential scanning calorimetry (DSC) was performed using a Netzsch DSC404 F1, by placing approximately 10 mg of nanoplatelet material in a quartz tube and sealed under vacuum of 10^{-3} Torr. An empty quartz tube was used as a reference. Both tubes were placed in the DSC, and the measurement was performed under flowing nitrogen gas from room temperature to 900 °C to determine phase purity and to identify thermal events that indicate phase changes. Scanning electron microscopy (SEM) using a Phillips XL-30 field emission gun was utilized to determine nanoplatelet morphology. Samples of nanoplatelets in ethanol were drop cast onto carbon tape for SEM characterization. Transmission electron microscopy (TEM, JEOL 2010F and JEOL 3100) and scanning transmission electron microscopy (STEM, JEOL 2100) were used to determine platelet lattice orientation and sub-micron features of materials. Both SEM, STEM, and TEM were equipped with EDAX electron dispersive spectroscopy (EDS) systems which were used for elemental mapping on the micron and nanometer scales. The Seebeck coefficient was measured from room temperature to 500°C under a low pressure He atmosphere using a commercial ZEM-3 system from ULVAC-RIKO. The instrument precision on the electrical resistivity and Seebeck coefficient data is $\pm 4\%$. The thermal conductivity was calculated from the thermal diffusivity data measured by the laser flash method (LINSEIS LFA 1000) from 30°C to 500°C under flowing N₂ gas (>30 mL/min).

References

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3. Rodriguez-Carvajal, J.; *Abstracts of the Satellite Meeting on Powder Diffraction of the XV Confress of the IUCr.* **1990**, 127.