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COMMUNICATION

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

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The use of template nanostructures for the creation of photovoltaic and thermoelectric semiconductors is becoming a quickly expanding synthesis strategy. In this work we report a simple two-step process enabling the formation of ternary CuAgSe nanoplatelets with a great degree of control over the composition and shape. Starting with hexagonal nanoplatelets of cubic Cu_{2-x}Se , ternary CuAgSe nanoplatelets were generated through a rapid ion exchange reaction at 300 K using AgNO_3 solution. The Cu_{2-x}Se nanoplatelet template and the final CuAgSe nanoplatelets were analyzed by electron microscopy and X-ray diffraction (XRD). It was found that both the low temperature pseudotetragonal and the high temperature cubic forms of CuAgSe phase were created while maintaining the morphology of Cu_{2-x}Se nanoplatelet template. Thermal and electronic transport measurements of hot-pressed pellets of the synthesized CuAgSe nanoplatelets showed a drastic reduction in the thermal conductivity and a sharp transition from n-type ($S = -45 \mu\text{V/K}$) to p-type ($S = +200 \mu\text{V/K}$) semiconducting behavior upon heating above the structural transition from the low temperature orthorhombic to the high temperature super-ionic cubic phase. This simple reaction process utilizing a template nanostructure matrix represents an energy efficient, cost-efficient, and versatile strategy to create interesting materials with lower defect density and superior thermoelectric performance.

Binary and multinary metal selenides have become important semiconductors for thermoelectric and photovoltaic applications. Much attention has been directed towards copper selenide compounds due to the large variety of copper selenide polymorphs that exists either naturally or synthetically.¹⁻⁸ In particular, the cubic phases of copper-lean, CuSe_2 , and copper-rich, Cu_{2-x}Se , are of interest for use as template lattice structures for the formation of desirable ternary and quaternary compounds.

Utilizing the room temperature metastable cubic structures of these phases as template structure can reduce the energy necessary to form compounds with complex chemical compositions while maintaining the high crystal symmetry and low defect densities, critical for photovoltaic and thermoelectric applications. Further, the stability of the selenium anionic sublattice can enable the creation of new materials that cannot be synthesized by conventional high temperature solid-state reactions.

CuAgSe was first synthesized by Miyatani et al. in 1973 and was shown to exist in two polymorphs: a low temperature β -phase that features a pseudotetragonal, or orthorhombic, structure (space group $P4/nmm$), and a high temperature superionic α -phase that exhibits a cubic structure (space group $Fm\bar{3}m$).⁹ The pseudotetragonal CuAgSe phase consists of alternating layers of Ag and CuSe. This structure favors high mobility of Ag^+ ions. Transition to the high temperature α -phase occurs at 523 K, and forms a very similar structure to superionic cubic Cu_2Se . The cubic phase consists of Ag^+ and Cu^+ cations randomly distributed at tetrahedral sites of the face centered cubic (fcc) unit cell of Se atoms. The transformation to this superionic phase of CuAgSe results in a dramatic drop in thermal conductivity, which is due to an increased disorder from random occupation of either Ag^+ or Cu^+ cations at atomic positions in the tetragonal structure.^{10,11} The thermoelectric properties of CuAgSe have not been extensively studied; however, the superionic nature of the α -phase coupled with the semimetal nature of the compound yields a great deal of interest due to low thermal conductivity and low electrical resistivity at higher temperatures. Nanostructuring of this material should dramatically increase the

figure of merit at high temperatures through increased phonon scattering, and quantum confinement of carriers.

In this work, we exploit the metastability at room temperature of the cubic Cu_{2-x}Se lattice to progressively replace the highly mobile Cu^+ cations by Ag^+ ions to form the ternary CuAgSe phase while maintaining the cubic structure as well as the nanoplatelet morphology. Two-dimensional (2D) morphology has been shown to increase the performance of thermoelectric materials by increasing the Seebeck coefficient through quantum confinement, as well as decreasing the thermal conductivity of the layered structure through phonon scattering at platelet boundaries.^{12,13} A two-step batch process consisting of the solvothermal synthesis of the Cu_{2-x}Se template material and a subsequent transformation by an ion exchange reaction appears to be an efficient and economic means to create nanoplatelets (NPs) of copper selenide-based ternary and quaternary compounds.

In an attempt to produce copper selenide NPs of both CuSe_2 and Cu_2Se compositions, the copper/selenium ratio in the solvothermal reactants were varied with a 1:2 and 1:1 molar ratio (Figure 1).¹⁴ The 1:1 molar ratio yielded a mixture of monoclinic and cubic Cu_{2-x}Se , while the selenium rich mixture produced pure cubic phase Cu_{2-x}Se (See Electronic Supplementary Information). Further attempts to synthesize CuSe_2 NPs by using larger excess of Se were unsuccessful under this experimental condition. Rietveld refinement using FullProf software was performed on XRD pattern of the sample with 1:2 Cu/Se ratio (pure cubic phase). The refinement yielded excellent fitting parameters ($R_f = 10.44$ and $\chi^2 = 3.52$) with a lattice parameter $a = 5.6332(2)$ Å and a stoichiometry of $\text{Cu}_{1.8}\text{Se}$.

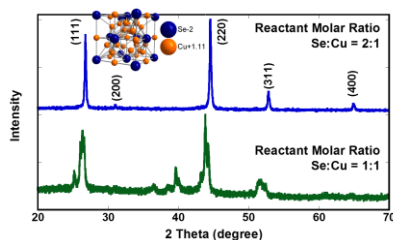


Figure 1: XRD patterns Cu_{2-x}Se NPs template obtained from solvothermal reaction. Both a molar ratio of Cu-Se of 1:2 and 1:1 of the reactants yielded Cu_{2-x}Se NPs, with the 1:2 ratio purely of the cubic phase. Cu_{2-x}Se structure shown in inset.

SEM secondary electron imaging revealed that the template material consists of NPs with widely varying size, from 500 nm to 3 μm in diameter, and from 50 – 91 nm in thickness (Figure 2.a). Transmission electron microscopy (TEM) studies showed that these platelets are indeed crystalline (Figure 2.b). Selected area electron diffraction (SAED) revealed the [111] direction normal to the planar surface of a single Cu_{2-x}Se NP. Scanning transmission electron microscopy (STEM) imaging indicated that the surface of the NPs is porous.

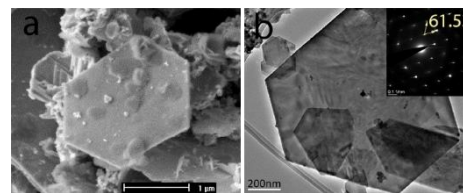


Figure 2: a) Secondary emission SEM image of Cu_{2-x}Se NP base material showing hexagonal platelet formation with thickness of 50-91 nm and diameter of 500 nm-3 μm . b) TEM image and SAED indicating [111] orientation of NP surface.

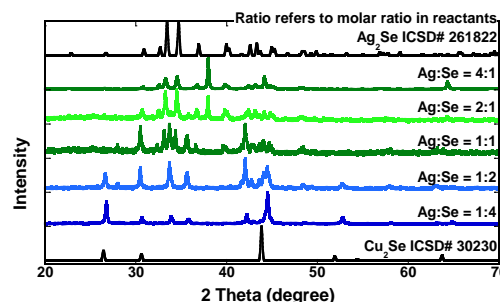


Figure 3: XRD patterns of ion exchange reaction products with varying molar ratios of silver to selenium in the reactants.

It is suggested that the porosity of these platelets is due to fast planar growth, which can be controlled by varying the NaOH concentration in the reactants.¹⁵

CuAgSe NPs were created via ion exchange reactions in ethanol at 300 K involving silver cations (Ag^+) and the synthesized Cu_{2-x}Se NPs. The molar ratio of Ag^+ cations to Se^{2-} anions in the starting mixture was systematically varied to achieve a single phase CuAgSe product. The Ag:Se molar ratio was initially varied from 1:4 to 4:1, and the products were analyzed with powder XRD (Figure 3). As predicted, increasing silver content in the ion exchange reaction increased the fraction $\text{Cu}_{2-x-y}\text{Ag}_y\text{Se}$ phases formed and the amount of copper cations (Cu^+) that were displaced. This is also indicated by the intensifying blue hue of the ethanol mixture (Figure 4). At a ratio of 1:4, the tetragonal and cubic phases of CuAgSe are formed, leaving a substantial portion of the template Cu_{2-x}Se NPs. At a ratio of 1:1, the undesirable tetragonal Ag_2Se phase is present, and at a ratio of 4:1, the entire product is a mixture of Ag_2Se and metallic Ag. It is therefore evident that at a molar ratio of four times the Ag^+ to Se^{2-} content in the reactants, all of the copper is replaced by silver cations. This result is contrary to work conducted by Lesnyak et al., which reports that a much larger excess, 50-100:1, of replacement cations is needed to fully transform the anionic template material.¹⁶

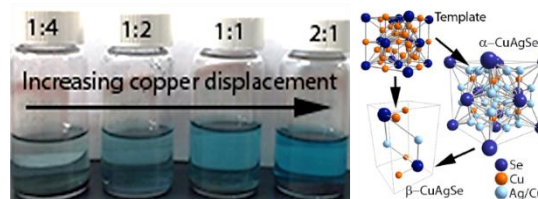


Figure 4: Increasing silver content in the ion exchange reaction displaces more copper cations (Cu^+) as indicated by the blue hue of the ethanol mixture. Ag:Se

ratio is shown on each vial. The large amount of β -CuAgSe formed is likely due to α -CuAgSe relaxing to the β phase after synthesis.

The ion exchange reaction was then optimized by varying the Ag:Se reactant ratio from 0.58 to 0.83 to achieve a pure CuAgSe product. XRD patterns from these products (Figure 5) indicate that a Ag:Se ratio of 0.67 to 0.75 yields a mixture of cubic and tetragonal CuAgSe with virtually no trace of the template material (Cu_{2-x}Se) or the undesirable material (Ag_2Se or metallic Ag). DSC measurements of the samples formed with Ag:Se ratios from 0.58 – 0.83 show endothermic events at 200 °C and 250 °C (Figure 6). These peaks are associated with the phase transition from β -CuAgSe (tetragonal) to α -CuAgSe (superionic) cubic phase. However, only the transition at 250 °C was reported in bulk CuAgSe sample.^{9,17,18} Although, the nanosizing of the CuAgSe platelets can have the effect of reducing the β to α phase transition, the mechanism by which particle size reduction alters solid-solid structural phase transitions is currently not well-understood.¹⁹

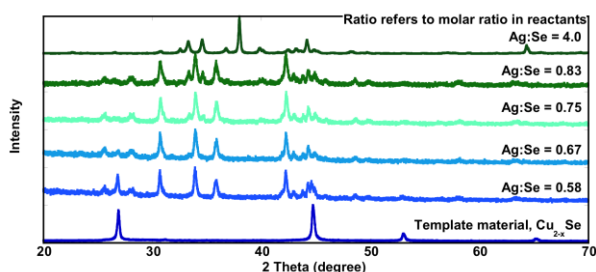


Figure 5: XRD patterns of ion exchange reaction products with Ag:Se molar ratio between 1:2 and 1:1 in order to achieve a pure CuAgSe product.

However, we speculate that the phase change near 200 °C, results from the high surface energy associated with very small NPs in the β phase. This is due to the fact that in the tetragonal phase, the cubic close packing structure of Se^{2-} ions in the NP is distorted from the energetically favorable [111] orientation. Therefore, the two phase-transition endothermic events on the DSC plots suggest that the ion exchange reactions result in the formation of CuAgSe NPs with a broad size distribution. This result is consistent with SEM analysis of the starting Cu_{2-x}Se NPs and is also supported by the disappearance of the endothermic event at 200 °C from the DSC curve during the second heating run.

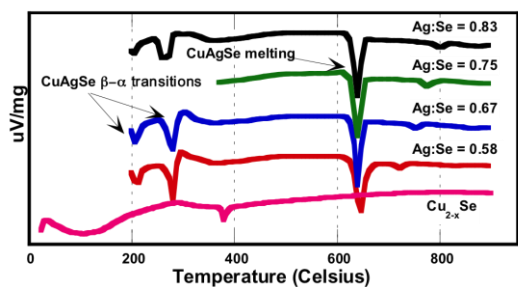


Figure 6: DSC data on heating of Cu_{2-x}Se and samples with Ag:Se ratio of 0.58-0.83 showing both β - α CuAgSe transition.

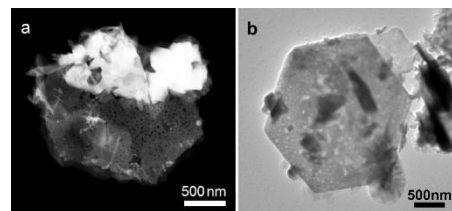


Figure 7: a) STEM image of Ag:Se = 1:2 sample showing that the hexagonal morphology of the template NP is maintained during ion exchange reaction. b) HRTEM image of Ag:Se = 1:1.

The DSC data shows that the material is mainly one phase and is stable until the onset of melting at 625 °C, which is substantially lower than the reported value of 780 °C for bulk CuAgSe.^{9,17} This melting point depression is associated with the reduction in particle size of CuAgSe NPs.¹⁹

It is particularly interesting to note the stabilization of the cubic phase of CuAgSe through ion exchange reaction at room temperature, which is far below the reported polymorphic transition temperature ($T_{\beta\alpha} > 200$ °C).¹⁷ We believe that the ability to form cubic CuAgSe phase at 25 °C through ion exchange reactions is favored by the use of the existing *fcc* structure of the Cu_{2-x}Se material as a lattice template (Figure 4). In addition, the similar of atomic arrangement of Se (*fcc*) in both cubic Cu_{2-x}Se and α -CuAgSe compounds, the high mobility of the copper cations in the cubic Cu_{2-x}Se superionic phase, and the porosity of the planar surface of the synthesized Cu_{2-x}Se NPs facilitate the ion exchange process between Cu^+ and Ag^+ ions at 300 K leading to the creation of cubic CuAgSe with low input energy.²⁰ The presence of a larger fraction of tetragonal CuAgSe in the final product indicate that the cubic CuAgSe is metastable under the reaction condition and partially transform to the more stable tetragonal lattice. This ion exchange method can therefore be used as a means to create metastable cubic ternary and quaternary phases of unique materials without the need for high temperature synthesis.

TEM and STEM methods were used to determine if the template morphology had been maintained after the formation of CuAgSe. STEM micrographs (Figure 7), showed that the hexagonal shape of the NPs were maintained for Ag:Se ratios of 1:2 and 1:1 with similar size distribution to the template NPs. EDAX using TEM showed that silver is distributed throughout the bulk of the NP somewhat uniformly, which indicated that the hexagonal NP consisted mainly of ternary phase material (Figure 8).

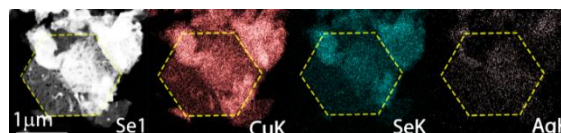


Figure 8: EDAX of NPs made with Ag:Se ratio of 0.67 showing silver cations distributed within the bulk of the NP, confirming that the Cu_{2-x}Se NP was transformed into CuAgSe phase.

CuAgSe NPs with tetragonal and cubic structures produced using a Ag:Se ratio of 0.71 were consolidated into pellets for thermal and electronic property measurements. A pellet suitable

for measurements was pressed at 450 °C with a pressure of 100 MPa for 2 hours, yielding a geometric density of 7.362 g/cm³ and a true density of 7.2339 g/cm³, 92% of the theoretical CuAgSe density (7.389 – 7.912 g/cm³).¹¹

Figure 9 shows the thermoelectric properties of the synthesized CuAgSe NPs. At 300 K, the total thermal conductivity is 2.7 W/mK and drastically decreases to 0.8 W/mK at the transition from the tetragonal β -CuAgSe to the cubic superionic α -CuAgSe structure. Further increase in the temperature resulted in the drop of the thermal conductivity to 0.4 W/mK at 775 K (Figure 9a). The observed sharp reduction of the thermal conductivity at the phase transition is ascribed to enhance phonon scattering due to the high degree of positional disorder and high mobility of Cu⁺ ions in the superionic cubic structure of α -CuAgSe. The total thermal conductivity of CuAgSe NP at various temperatures is comparable to that of bulk CuAgSe prepared by solid-state reaction of the elements.¹⁰

Temperature dependent thermopower data (Figure 9b) revealed negative values at temperatures below the transition from β - to α -CuAgSe, $T_{\beta\alpha}$, indicating electrons as majority charge carriers (n -type). The thermopower of β -CuAgSe gradually decreases with increasing temperatures from -50 μ V/K at 300 K to \sim -20 μ V/K at the vicinity of $T_{\beta\alpha} \sim$ 450 K and surprisingly jumps to a large positive value (+200 μ V/K) at a temperature slightly above $T_{\beta\alpha}$. This indicates holes as majority carriers (p -type) in α -CuAgSe. The thermopower continues to increase with temperature reaching a maximum value of +260 μ V/K at 675 K. The magnitude of S for the α -CuAgSe NPs is higher than that of bulk CuAgSe obtained by solid-state reaction of the elements.¹⁰ The observed sudden switch of the conduction type from n -type in β -CuAgSe to p -type in α -CuAgSe was also reported in polycrystalline CuAgS and CuAgSe.^{10,21} Such change in the conduction type can be associated with the alteration of the electronic structure of CuAgSe due to atomic rearrangement in the β and the α polymorphs.²² At 300 K the electrical resistivity of CuAgSe NPs is $5.7 \times 10^{-4} \Omega \text{ cm}$ and increases with temperature to $\sim 1.9 \times 10^{-3} \Omega \text{ cm}$ at a temperature slightly below $T_{\beta\alpha}$. This behavior is consistent with heavily doped semiconducting behavior. The electrical resistivity suddenly increases to $1.5 \times 10^2 \Omega \text{ cm}$ slightly above $T_{\beta\alpha}$. This increase in the electrical resistivity is ascribed to a large drop in the overall carrier mobility, due to (1) the change in the majority carrier type from high mobility electrons to low mobility holes and (2) enhanced carrier – impurity scattering arising from the superionic behavior of Cu and Ag ions in Cubic CuAgSe. Above $T_{\beta\alpha}$, the electrical resistivity continues to increase with rising temperature indicating heavily doped p -type semiconducting behavior. The thermoelectric figure of merit, ZT, calculated from the above data is shown in Figure 8b. At 300 K, the ZT value is \sim 0.05 and remains nearly constant up to the β to α transition, $T_{\beta\alpha}$. Above $T_{\beta\alpha}$, the ZT values of the p -type α -CuAgSe phase rapidly increases with temperature reaching \sim 0.55 at 700 K.

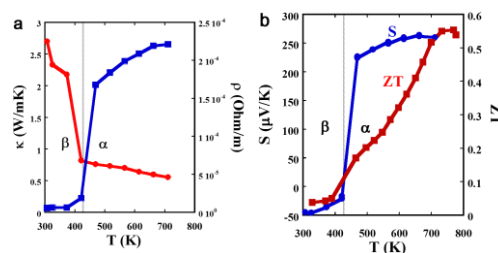


Figure 9: a) Temperature dependent thermal conductivity and electrical resistivity of a high-density pellet of CuAgSe NPs showing a sharp drop in the thermal conductivity at the transition from β - to α -CuAgSe. b) Temperature dependence of the Seebeck and ZT, revealing a switching from n -type semiconducting behaviour in β -CuAgSe to p -type in α -CuAgSe.

Although this number is slightly lower than the value reported for bulk CuAgSe,⁹ it indicates that CuAgSe NPs with promising thermoelectric performance can be fabricated easily at 300 K using a simple and rapid ion exchange reaction between Cu₂Se and Ag⁺ salt.

Conclusions

In conclusion, we report a simple and rapid strategy for the fabrication of both β -CuAgSe (pseudotetragonal) and α -CuAgSe (cubic) NPs at 300 K. Starting from cubic Cu_{2-x}Se NPs template, β -CuAgSe and α -CuAgSe NPs were successfully created at 300 K through partial exchange of Cu⁺ ions in Cu_{2-x}Se template by ion Ag⁺ ions while maintaining the original morphology of the Cu_{2-x}Se NPs. By varying the ratio of Ag:Se content in the ion exchange reaction we were able to control the composition of the product NPs, and fully transform the Cu_{2-x}Se platelets to Ag₂Se. Electronic and thermal transport properties of CuAgSe NPs consolidated by hot-pressing showed low thermal conductivity, high thermopower and moderate electrical resistivity at high temperatures leading to a ZT value of 0.55 at 700 K. This work demonstrates that the aforementioned simple two-step batch process could potentially be used for cost-efficient and energy efficient fabrication of NPs of various materials suitable for thermoelectric, photovoltaic, and spintronic applications.

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Table of contents entry

High Cu^+ mobility in cubic Cu_{2-x}Se facilitates Cu^+ and Ag^+ ion exchange leading to the creation of cubic CuAgSe at 300K.

