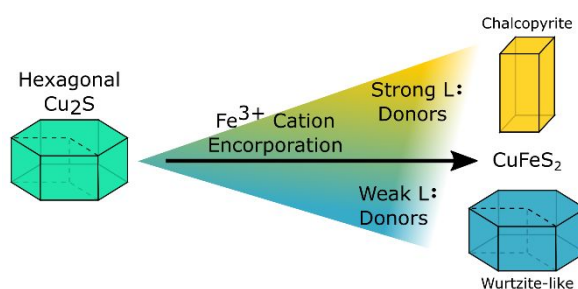


Tolman's Electronic Parameter of the Ligand Predicts Phase in the Cation Exchange to CuFeS₂ Nanoparticles

Christopher G. Sharp,^{†,‡} Alice D. P. Leach,[‡] and Janet E. Macdonald^{†,‡,*}

[†]Department of Chemistry and [‡]Vanderbilt Institute of Nanoscale Science and Engineering, Vanderbilt University, Nashville, Tennessee 37235, United States

ABSTRACT: The metastable and thermodynamically favored phases of CuFeS₂ are shown to be alternatively synthesized during partial cation exchange of hexagonal Cu₂S using various phosphorus-containing ligands. Transmission electron microscopy and Energy dispersive spectroscopy mapping confirm the retention of the particle morphology and the approximate CuFeS₂ stoichiometry. Powder X-ray diffraction patterns and refinements indicate that the resulting phase mixtures of metastable wurtzite-like CuFeS₂ versus tetragonal chalcopyrite are correlated with the Tolman electronic parameter of the tertiary phosphorous-based ligand used during the cation exchange. Strong L-type donors lead to the chalcopyrite phase, and weak donors to the wurtzite-like phase. To our knowledge, this is the first demonstration of phase control in nanoparticle synthesis using solely L-type donors.



KEYWORDS: nanocrystal, metastable phase, cation exchange, chalcopyrite, wurtzite, Tolman electronic parameter

Crystallographic polytypes give opportunities for diversification of material properties without changing composition. In nanomaterials, the cubic/hexagonal polytypism was first exemplified with the II-VI semiconductors such as CdSe and CdS in which both polytypes were both known as bulk materials.¹⁻³ In more recent years, nanocrystal synthesis has led to the discovery of novel crystal phases in other materials where previously only one of the hexagonal or cubic phases were known in the bulk.⁴⁻¹¹

Ternary I-III-VI₂ semiconductor nanocrystals are potential less-toxic replacements of the cadmium and lead chalcogenide nanocrystals. Their diversity of composition allows for tunability of their band gaps and other physical properties. Furthermore, when cation poor, these semiconductors often possess surface plasmon resonances centered in the NIR portion of the spectrum. Many of the I-III-VI₂ semiconductors have chalcopyrite (CP) thermodynamic phases: crystal structures based on a doubled unit cell of cubic zinc blende to accommodate ordering of the two cations. However, metastable wurtzite-like (WZ-like) analogous polytypes, not known in the bulk, have also been prepared in colloidal nanocrystal (NC) preparations. Examples include CuInS₂, CuInSe₂, and CuGaO₂.⁵⁻¹¹ These new polytypes present a further field of diversity of semiconductor properties, including an inherent asymmetry built into a hexagonal crystal structure, in which the crystallographic c-direction is chemically and electronically unique to the a- and b-directions.

Our research group strives to understand why unique metastable products form in nanocrystal syntheses, not

only to achieve reproducibility, but also to provide the synthetic framework to facilitate the syntheses of other novel crystallographic phases through bottom-up synthesis. Here we add to this body of work, exploring the phase-controlled synthesis of CuFeS₂ and present a novel wurtzite-like (WZ-like) phase. A hexagonal analogue of CuFeS₂ is particularly interesting because as an inherently anisotropic material, it may have present advantages in thermoelectric, photocatalytic and electrochemical applications over the already promising chalcopyrite phase.^{12,13} Here we also illustrate how ligand environment influences phase in partial cation exchange processes to metastable phases. Here, "partial" is used to denote that not all the Cu is removed from the particles in the reaction rather than to imply an incomplete reaction to the product CuFeS₂ phases.

It has been observed previously that ligand choice in colloidal syntheses is imperative to polytype control.¹⁴⁻¹⁷ In the case of well-studied CdSe, ligand choice has been shown to change the rate of the reaction, preventing or creating stacking faults and other defects during crystal growth that can catalyze transformations between metastable and thermodynamic polytypes.¹⁸ It has also been observed that strong anionic X-type ligands such as phosphonate and oleate stabilize cubic CdSe with its four, equivalent, cation-rich [111] facets. The hexagonal wurtzite phase has only one cation-rich [200] facet and so is preferred under conditions dominated by neutral L: type donors such as amines.¹⁵

In the phase control of the I-III-VI semiconductor nanocrystals, ligands have been shown to also control phase, but through a differing mechanism. The role of

ligands such as 1-dodecanethiol is to influence the formation of phase-directing intermediate nanocrystals.¹⁹ In this case, the 1-dodecanethiol plays a special role as a reagent at high temperatures, becoming a sulfur source. Under these conditions, hexagonal Cu_2S forms as an intermediate, and becomes a cation exchange host to WZ-like Cu-III- S_2 products.^{20,21} Similarly, Brutchey showed that the phase control of nanocrystals of chalcopyrite of WZ-like CuInSe_2 forms though specific copper selenide intermediates.^{10,22}

The conservation of the structure of the anionic sublattice has been an underpinning feature of cation exchange in general, and is now a well-established route to metastable phases of nanomaterials.^{23,24} It is important to note that the phase control of the second cation-exchange step to ternary materials has been previously thought to be relatively independent of the ligand environment. In contrast, here we show that the phase of the CuFeS_2 product of cation exchange is not impervious to ligand environment even at room temperature. From the same hexagonal Cu_2S starting point, the WZ-like/CP phase composition of the product has a linear relationship with the Tolman Electronic Parameter (TEP) of added phosphines and phosphites; Strongly donating phosphines lead to the thermodynamic chalcopyrite phase, and weakly donating phosphines allow for the maintenance of the hexagonal anion lattice and the formation of the metastable wurtzite-like CuFeS_2 phase (Figure 1). In comparison to the use of ligands to influence the phase of CdSe , here, all the phosphine ligands are strictly L-type.^{12,13,25} This brings into question the hypothesis that anionic X-type ligands are needed to stabilize many charged facets to influence structural transformations to cubic and cubic-like phases.

Among I-III-VI₂ semiconductors, CuFeS_2 has been studied extensively in its thermodynamically favored tetragonal phase. Chalcopyrite (CP) has seen application in solar cells, lithium-ion batteries, and thermoelectrics.^{12,26} Metastable CuFeS_2 may offer a greater degree of electronic control due to the propagation of electron flow in anisotropic directions commonly seen in hexagonal rather than cubic structures.²⁷⁻²⁹ The three reported syntheses of metastable CuFeS_2 have focused on kinetic approaches by manipulating nucleation temperatures and reaction temperature ramp rates.^{12,13,25} Rather than a one-pot synthesis, here we employ a partial cation exchange (CE) of hexagonal Cu_2S to produce WZ-like CuFeS_2 , in a method analogous to those performed for CuInS_2 .^{20,30,31} The two-step method provides opportunity for detailed study of the mechanisms of phase control.

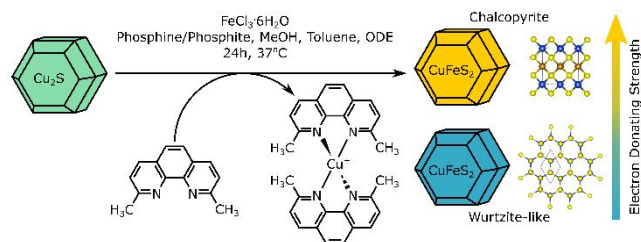


Figure 1. Schematic of the synthesis used to exchange Cu_2S into tetragonal and WZ-like CuFeS_2 particles.

Cu_2S seed particles were prepared through a literature procedure by heating $\text{Cu}(\text{acac})_2$ in 1-dodecanethiol. The

resulting Cu_2S nanocrystals (13.96 ± 0.83 nm, $n = 200$) had the low chalcocite crystal structure (Figure 2) with a pseudo hexagonal anion sublattice. These nanocrystals were the host materials for cation exchange to CuFeS_2 . The method of utilizing the Cu_2S seed anion sublattice to template the metastable hexagonal crystal phase in the product allows for a wide variety of products of the ternary material with regard to size and morphology. Cu_2S nanocrystals in the literature include spheres ranging from 2 to 20 nm spheres as well as rods.^{27,29,32-34}

The synthesis of CuFeS_2 was performed by stirring a toluene solution of host Cu_2S nanocrystals with FeCl_3 dissolved in MeOH. Neocuproine was added to help drive the cation exchange forward, as it is known as a very strong, selective chelator for $\text{Cu}(\text{I})$.³⁵⁻³⁷ Under the conditions reported in the SI, the cation exchange required stirring overnight. As an aside, halving the concentration of all components increased the reaction time to several days, up to a week. As a last component, amines, phosphines or phosphites were added as surface stabilizing ligands (Figure 1) which unexpectedly were instrumental in controlling the phase of the CuFeS_2 product.

All products were characterized with powder X-ray diffraction (pXRD) (Figure 2a). When strongly donating phosphines such as tributyl phosphine were employed, the resultant nanoparticles showed the thermodynamic chalcopyrite phase of CuFeS_2 . In the presence of the weakest donating phosphine, triphenyl phosphite, the product nanoparticles produced a diffraction pattern similar to wurtzite-like polytypes, such as CuInS_2 or $(\text{Cu}(\text{I})\text{P})\text{S}_2$ and was consistent with the few patterns reported for a WZ-like phase of CuFeS_2 NC.^{12,13,25,38,39} (Figure 2) The pattern was refined to a WZ unit cell with dimensions of $a = 3.70\text{\AA}$, $c = 6.12\text{\AA}$, with a hcp packed sulfur lattice and 50% occupancy of the tetrahedral holes by an equal ratio of Cu and Fe cations. This unit cell was chosen for simplicity, despite the likelihood that the structure supports a lower symmetry and cation ordering, or even several types of cation ordering as has been seen in aberration corrected STEM for WZ-like CuInS_2 nanocrystals.⁵

Phosphorus ligands with intermediate electron donating abilities produced a mixture of phases. Resulting phase compositions were determined using Rietveld refinement (SI for details) and found to agree well with varying percent compositions of wurtzite-like and tetragonal patterns. The percent composition was plotted against the TEP of the ligand- which gives a quantifiable measure of electronic donation based on CO stretching frequencies of $\text{NiL}(\text{CO})_3$ complexes, where L is a phosphine/phosphite ligand.⁴⁰ Low CO stretching frequencies are indicative of a strongly donating ligand. A clear linear correlation between the electron donation strength and the % chalcopyrite was observed (Figure 2b).

This linear relationship between TEP and product phase composition allowed for high phase tunability of the product. Additionally, this trend allows us to qualitatively compare the electronic donation properties of phosphite and phosphorous ligands with low steric bulk that were never tested by Tolman. For example, trioctylphosphine produces a percent composition of CuFeS_2 phase

intermediate to $P(\text{Et})_3$ and $P(\text{Bu})_3$ and so a TEP of $\sim 2061 \text{ cm}^{-1}$ can be extrapolated.

In all cases, TEM of the CuFeS_2 particles indicated that they retained the sphere-like morphology of the Cu_2S host, but shrunk significantly. A lattice volume contraction of $\sim 23\%$ is to be expected, based on the unit cells of chalcocite, WZ-like and CP CuFeS_2 phases, which equates to a reduction of diameter by 8.5%. Upon cation exchange from Cu_2S to CuFeS_2 , a larger decrease in particle diameter of 14–36 % was observed, with the particles prepared in the presence of strongly donating phosphines being the smallest. It can be concluded that in addition to the lattice contraction, the strong phosphines are etching the Cu_2S precursor, similar to that observed by the Robinson Group.⁴¹ Cation exchange of seed particles that were only 10 nm ($\sim 25\%$ smaller) did not cause a noticeable difference in the resultant phase ratio. Size effects on phase control can be excluded as an explanation from this system.

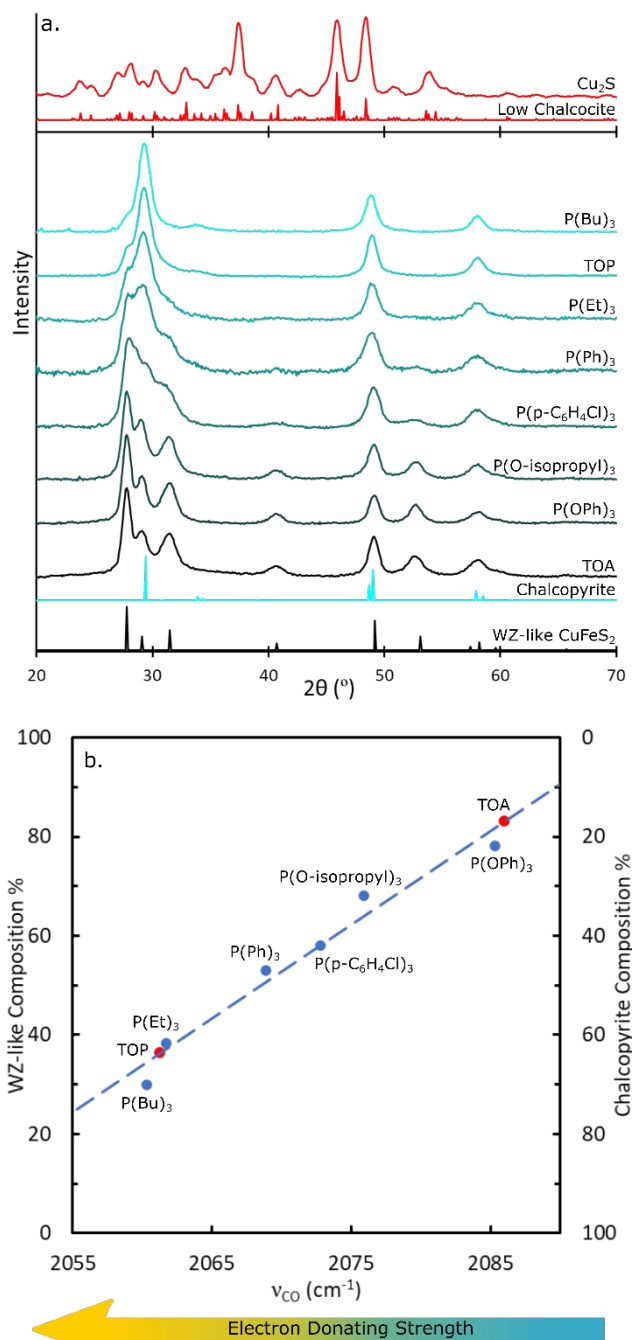


Figure 2. PXRD of CuFeS_2 products exchanged in the presence of varying phosphorous based ligands. The resulting products had their percent phase composition analyzed using Rietveld refinements and the resulting compositions graphed in relation to the electron donating tendencies of the coordinating ligand as measured by Tolman et al.

Quantitative EDS indicated that the cation composition of the particles was close to stoichiometric 1:1 Cu:Fe (Figure 3). It was noted that in the presence of the strongest donating phosphines, the particles were cation rich with a stoichiometry of $\text{Cu}_{1.0}\text{Fe}_{1.0}\text{S}_{1.6}$. This is consistent with the observations of the Robinson group that phosphines preferentially etch the sulfur of copper(I) sulfides. In the presence of weakly donating triphenylphosphite, the sulfur

content remained high with resultant composition of $\text{Cu}_{1.1}\text{Fe}_{1.0}\text{S}_{2.1}$.

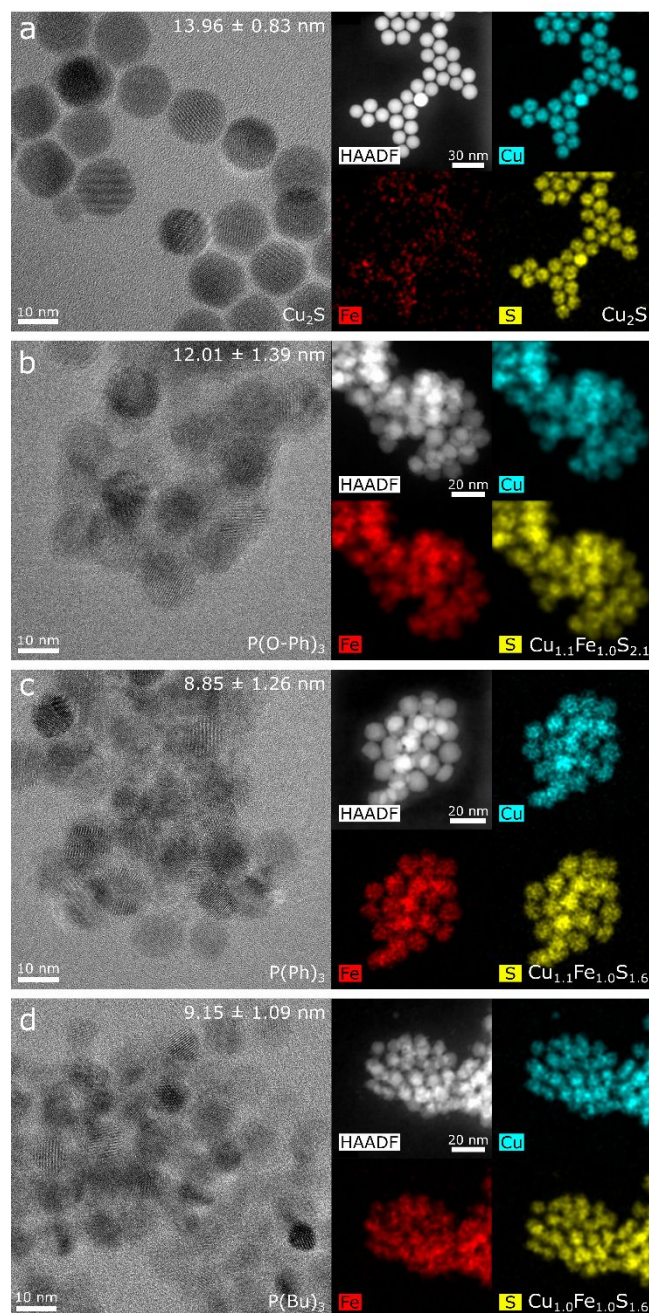


Figure 3. TEM and TEM-EDS images acquired of CuFeS_2 at either phase extreme of (a) WZ-like, (b) mixed phase, and (c) tetragonal products. EDS shows cation rich product as CuFeS_2 becomes less WZ-like as the phosphorous ligands become more electron donating.

HR-TEM of the product nanoparticles demonstrated that the WZ-like CuFeS_2 particles were single crystalline, as is expected from cation exchange with a retained anion sublattice. However, the CP particles were polycrystalline, indicating a major anion reorganization and recrystallization into the FCC stacking of sulfur anions occurs from several points in each nanoparticle (Figure 4).

At first pass, the observed trend that strongly donating ligands prefer the tetragonal phases seems to agree with the

existing phase control literature on CdSe quantum dots. Huang *et al.*, observed that strong anionic ligands favored the cationic four [111] surfaces of zincblende CdSe NCs, directing the phase in syntheses to the cubic phase.¹⁵ Indeed, our observations on stoichiometry seem to agree; the CP CuFeS_2 particles formed are cation rich, perhaps suggesting cation rich surfaces, whereas the WZ particles are stoichiometric. What is most curious is that the existing literature observations with CdSe indicate that the ZB directing ligands must be X-type and the WZ directors L-type. Instead here, both directing ligands are L-type. Such a discrepancy with the prevailing logic requires further investigation.

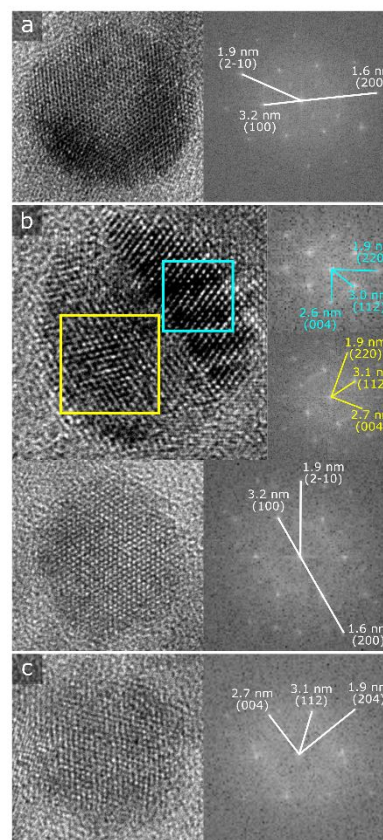


Figure 4. HRTEM of and FFT of particles of (a) WZ-like phase obtained in the presence of weakly donating triphenylphosphite and (b) both phases obtained in the presence of intermediate donating triphenylphosphine. Particles that exhibited the CP phase were polycrystalline (top) yet those that showed the WZ-like phase were single crystalline (bottom). Mixed-phase particles were not readily observed. (c) Chalcopyrite was produced in the presence of strongly donating trioctylphosphine (TOP).

Existing literature has emphasized the role of ligands stabilizing specific ion rich facets in different crystal phases, which has been used to selectively produce cubic and hexagonal phases both during and in post synthetic steps.^{14-17,19} Mahler, Lequeux and Dubret *et al.* noticed that heating pre-formed ZB-CdSe NCs at 200°C in excess L-type oleylamine could induce a phase transition to WZ.¹⁴ Similar annealing experiments by Talapin *et al.* in high purity L-type TOPO showed transformations of ZB CdSe to the WZ phase.

As a counter point, heating WZ CdSe the addition of X-type alkyl phosphonates promoted the partial transformation of WZ NCs to ZB.¹⁵

To test if CuFeS_2 polytypism is sensitive to similar particle surface stabilization as CdSe nanocrystals, we examined if phase can be tuned post-synthetically. Both WZ-like and mixed phase CuFeS_2 samples were stirred in the presence of excess strongly-donating PBu_3 to see if post-synthetic phase conversion was possible. Under synthetic conditions, the transformation of the anion lattice from WZ-like to cubic to yield the CP phase occurs in the presence of PBu_3 , but under these post-synthetic conditions, the resulting products did not indicate any change in phase composition by pXRD (Supporting Information). A substantial activation energy between the WZ-like and CP phases must therefore exist, and more importantly, the event of cation exchange is critical to the phase control of this reaction.

Further attempts at post-synthetic phase conversion were performed using a high temperature pXRD furnace to further rule out thermal interconversion between the phases. Metastable WZ-like CuInS_2 will convert to the thermodynamically stable CP phase between 400°C and 500°C, whereas the metastable WZ Cu_2Se phase transforms to the cubic at only 150°C.⁷ WZ-like CuFeS_2 nanocrystals that were synthesized through cation exchange in the presence of amine ligands were heated to 500°C. pXRD patterns were taken at room temperature and every 100 degrees starting at 100°C (Figure 5). Thermal stability of the WZ CuFeS_2 to 300°C was observed, whereupon it oxidized. This temperature is similar to the oxidation of chapcolyrite ores, but the oxide products were different.⁴² Such temperature stability, and high activation energy for phase transformation between the metastable WZ and CP phases further indicates that the event of cation exchange is crucial to phase control.

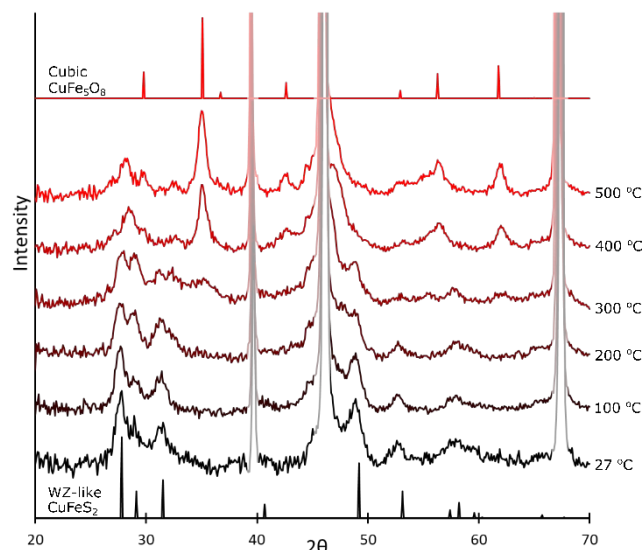


Figure 5. Temperature-dependent pXRD of WZ-like CuFeS_2 NCs. Reflections by the platinum sample holder signals at approximately 39, 47 and 67° 2θ have been faded.

An alternative hypothesis to a dominating role of particles surface stabilization, is that the differing strength of the phosphines influences the relative reactions rates in

the cation exchange. Poorly matched rates cause a high density of defects that can catalyze a phase transformation. In the cation exchange to CuFeS_2 , there is both the rate at which Cu^+ is removed from the lattice and the rate in which Fe^{3+} is incorporated. In the presence of weakly donating phosphines, FeCl_3 methanol solutions displayed only the charge transfer bands and yellow color of typical of FeCl_3 solutions that are d^5 high-spin, with no spin allowed transitions. However, in the presence of a strongly donating phosphine, such as Bu_3P , the solution turned a deep purple indicating a coordination with the phosphine and d^5 low-spin configuration with spin allowed d-d transitions (Supporting information).⁴³ The strong coordination of the ferric ions by the strongly donating phosphines slows their incorporation into the crystal lattice compared to the rate at which Cu^+ is extracted and coordinated by neocuproine. This imbalance in rates, causes a transient high concentration of cation vacancy defects that catalyze the product to convert to its more energetically favored phase, CP. This mechanism would conform with the kinetic arguments proposed originally by Ostwald and since used to grow large nanoparticles in metastable phases by selecting synthetic conditions that prevent the formation of defects that catalyzed the phase transition.^{18,44} A corollary observation has been made by Steimle et al, who noticed that phosphines can induce lattice sulfur vacancies that catalyze the transformation of $\text{Cu}_{1.8}\text{S}$ digenite (fcc-like sulfur lattice) to Cu_2S Chalcocite (hcp-like sulfur lattice) prior to cation exchange to ZnS. Here, under the same phosphines, the opposite transformation of the anion lattice is observed in the cation exchange to CuFeS_2 .⁴⁵

A test of this kinetic hypothesis is to examine closely the samples that exhibited both WZ-like and CP phases under intermediate phosphine strength. In a thermodynamically controlled process where surface energies are minimized by those presented by the CP phase, individual particles might be expected to exhibit both CP and WZ phases in some sort of equilibrium with clean, low-energy, epitaxial interfaces.^{2,46} However, if the conversion process is event driven and kinetically determined, one would expect that individual particles express either WZ or CP phase, not both; under these intermediate conditions, not all particles experience the event that catalyzes the transformation from hexagonal the cubic. In the particles observed by HR-TEM, it was noted that these samples contained particles that were entirely WZ-like phase, or particles that were polycrystalline CP with many faults. Particles exhibiting both phases were not readily observed (Supporting information). Therefore, the HR-TEM further supports a kinetic interpretation of the phase control. The individual particles can be thought of as their own reactors. The observations of mixed- phase products containing individual all-WZ and all-CP particles suggest a stochastic formation of catalyzing vacancies across the myriad of particles.

Lowering the transient concentration of vacancies prevents the phase conversion to CP. Besides changing the identity of the iron-binding phosphine, increasing the availability of free Fe^{3+} by lowering the phosphine concentration should also increase the amount of WZ-like product. Indeed, when the concentration of intermediate

binding PPh_3 was lowered from 8.5 eq to 1 eq (to iron), the product diffraction pattern resembled what would be expected if the weaker donating $\text{P}(\text{p-C}_6\text{H}_4\text{Cl})_3$ were used, instead. (supporting information, and figure S4)

Here presented is the phase-controlled synthesis of CuFeS_2 through partial cation exchange from Cu_2S . Weakly donating ligand environments during cation exchange were found to favor the metastable WZ-like phase, retaining the hexagonal anion sublattice of the host Cu_2S . Strong donor environments gave the thermodynamic CP phase. Phase composition of the product has a linear relationship with the ligand Tolman Electronic Parameter.

To our knowledge, this is the first instance of phase control using L-type ligands of the same coordinating head, which is in contrast to previous phase-control work with CdSe where X vs. L-type ligands were needed to influence phase between cubic and hexagonal structures. The previous work suggests a thermodynamic stabilization of ligand surfaces influence phase. Here, the effect is kinetic. We hypothesize the ligands effect the rates of exchange of the two cations. Transient defects when the rates are imbalanced catalyze the transformation of the anion sublattice to the thermodynamic CP phase. Once formed, the metastable WZ- CuFeS_2 was thermally stable and, upon heating, oxidized between 300-400°C rather than converting to the CP phase.

These experiments demonstrate that the process of cation exchange and partial cation exchange can be highly destabilizing to the anion sublattice, and that ligand environment can be chosen carefully – even within one ligand class – to stabilize the process. The mechanisms of how ligands influence phase in direct syntheses to binary materials are not the same as those in cation exchange processes. The experiments will help the further synthesis of novel metastable materials, especially ternary semiconductors through cation exchange processes, with prospects in thermoelectric generators and other electrochemical applications.

ASSOCIATED CONTENT

The Supporting Information is available free of charge on the [ACS Publications website](#) at DOI:

Reagents and vendors; preparation of Cu_2S hosts and CuFeS_2 products; instrumentation parameters; pXRD phase refinements; pXRD of the products of further phase control experiments through ligand concentration; UV-vis of solution of FeCl_3 and phosphorous ligands; further HRTEM of CuFeS_2 products. (PDF)

AUTHOR INFORMATION

Corresponding Author

Janet E. Macdonald Department of Chemistry and Vanderbilt Institute of Nanoscale Science and Engineering, Vanderbilt University, Nashville, Tennessee 37235, United States.

Email: janet.macdonald@vanderbilt.edu

Author Contributions

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