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Tolman's Electronic Parameter of the Ligand Predicts Phase in the Cation Exchange to $CuFeS_2$Nanoparticles

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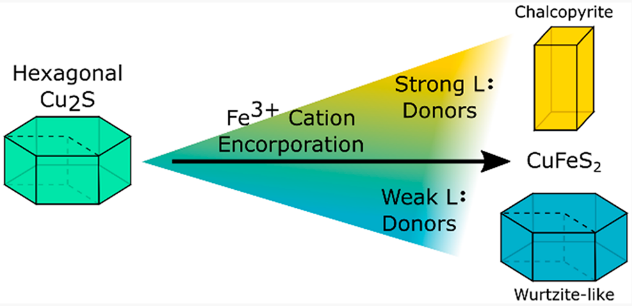
ABSTRACT: The metastable and thermodynamically favored phases of $CuFeS_2$ are shown to be alternatively synthesized during partial cation exchange of hexagonal Cu_2S using various phosphorus-containing ligands. Transmission electron microscopy and energy dispersive spectroscopy mapping confirm the retention of the particle morphology and the approximate $CuFeS_2$ stoichiometry. Powder X-ray diffraction patterns and refinements indicate that the resulting phase mixtures of metastable wurtzite-like $CuFeS_2$ versus tetragonal chalcopyrite are correlated with the Tolman electronic parameter of the tertiary phosphorus-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−VI_2 semiconductor nanocrystals are potential less-toxic replacements of 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−VI_2 semiconductors have chalcopyrite (CP) thermodynamic phases, that is, 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 $CuInS_2$, $CuInSe_2$, and $CuGaO_2$.[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 $CuFeS_2$ and present a novel wurtzite-like (WZ-like) phase. A hexagonal analogue of $CuFeS_2$ 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 the phase in partial cation exchange processes to metastable phases. Here, "partial" is used to denote that not all of the Cu is removed from the particles in the reaction rather than to imply an incomplete reaction to the product $CuFeS_2$ 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

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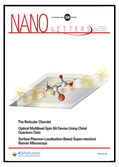

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CdSe with its four, equivalent, cation-rich [111] facets. The hexagonal wurtzite phase has only one cation-rich [200] facet and so is preferred under conditions dominated by neutral L-type donors such as amines.[15]

In the phase control of 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 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−VI_2 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.

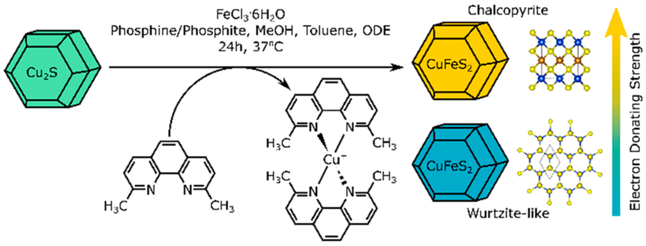

Figure 1. Schematic of the synthesis used to exchange Cu_2S into tetragonal and WZ-like $CuFeS_2$ particles.

Cu_2S seed particles were prepared through a literature procedure by heating $Cu(acac)_2$ 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

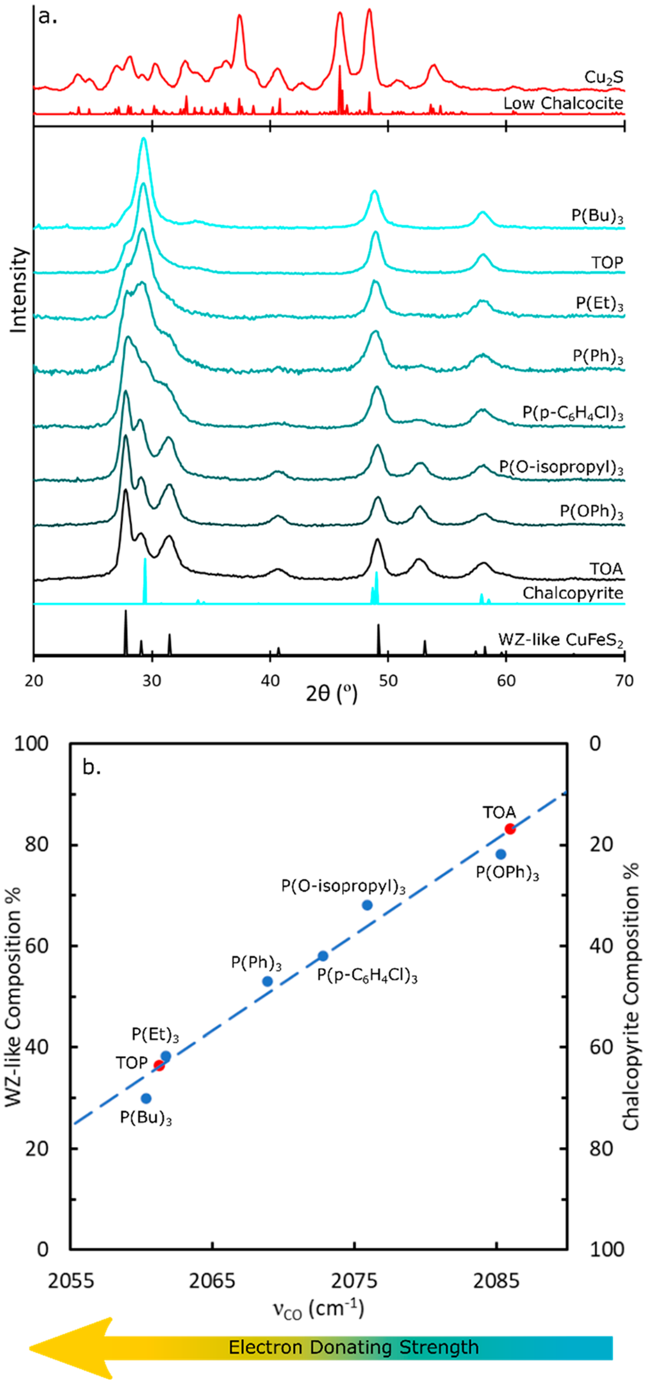

Figure 2. PXRD of $CuFeS_2$ products exchanged in the presence of varying phosphorus-based ligands. The resulting products had their percent phase composition analyzed using Rietveld refinements and the resulting compositions graphed in relation to the electron donating tendencies of the coordinating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

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 Cu(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 $(Cu(I)P)S_2$, 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 $a = 3.70$ Å, $c = 6.12$ Å with an 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 $NiL(CO)_3$ 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 phosphorus ligands with low steric bulk that were never tested by Tolman. For example, trioctylphosphine produces a percent composition of $CuFeS_2$ phase intermediate to $P(Et)_3$ and $P(Bu)_3$ and so a TEP of ~2061 cm^{-1} can be extrapolated.

In all cases, TEM of the $CuFeS_2$ particles indicated that they retained the spherelike morphology of the Cu_2S host but shrunk significantly. A lattice volume contraction of ~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 (~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.

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 $Cu_{1.0}Fe_{1.0}S_{1.6}$. This is consistent with the observations of the Robinson group that phosphines preferentially etch the sulfur

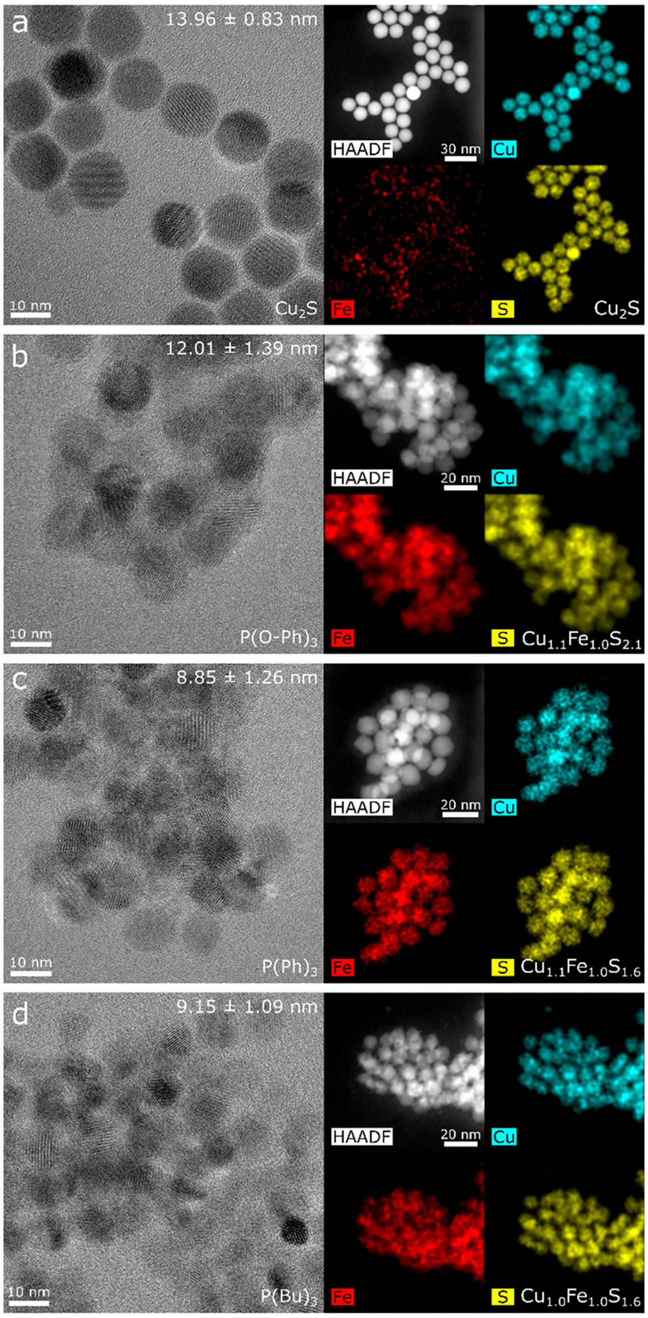

Figure 3. TEM and TEM-EDS images acquired of $CuFeS_2$ at either phase extreme of (a) WZ-like, (b) mixed phase, and (c) tetragonal products. EDS shows the cation rich product as $CuFeS_2$ becomes less WZ-like as the phosphorus ligands become more electron donating.

of copper(I) sulfides. In the presence of weakly donating triphenylphosphite, the sulfur content remained high with resultant composition of $Cu_{1.1}Fe_{1.0}S_{2.1}$.

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 must be L-type. Instead, here both directing ligands are L-type. Such a discrepancy with the prevailing logic requires further investigation.

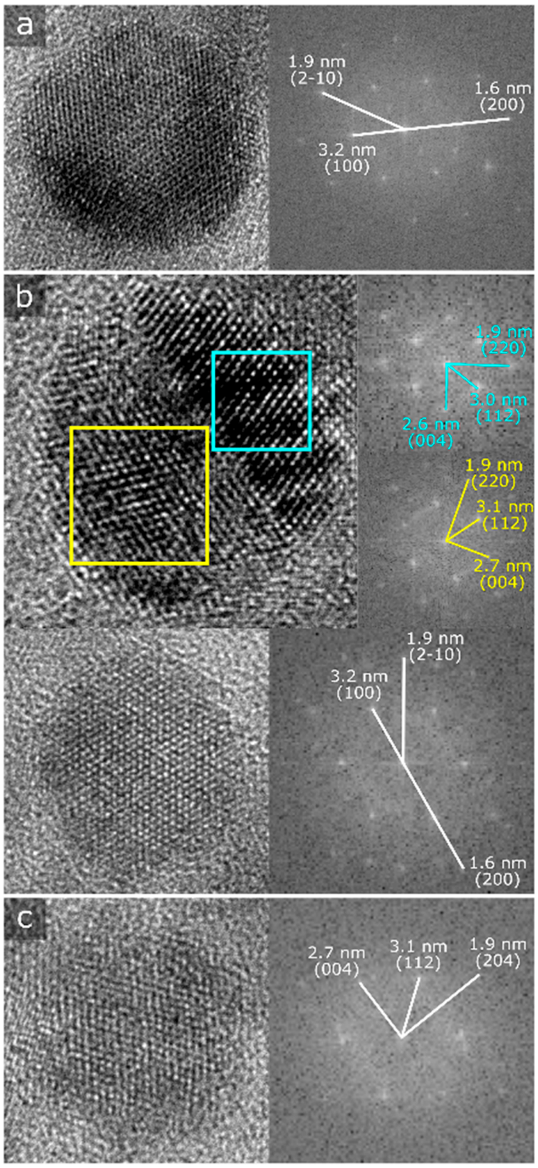

Figure 4. HRTEM of and FFT of particles of (a) WZ-like phase obtained in the presence of weakly donating triphenylphosphite and (b) both phases obtained in the presence of intermediate donating triphenylphosphine. Particles that exhibited the CP phase were polycrystalline (top) yet those that showed 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 Dubertret et al. noticed that heating preformed 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.[15] As a counterpoint, when 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 postsynthetically. Both WZ-like and mixed phase $CuFeS_2$ samples were stirred in the presence of excess strongly donating PBu_3 to see if postsynthetic 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 postsynthetic 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 postsynthetic 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 and 500 °C, whereas the metastable WZ Cu_2Se phase transforms to the cubic at only 150 °C.[7,42] 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° 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.[43] Such temperature stability and high activation energy for phase transformation between the metastable WZ and CP phases further indicate that the event of cation exchange is crucial to phase control.

An alternative hypothesis to a dominating role of particle 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+} in incorporated. In the presence of weakly donating phosphines, $FeCl_3$ methanol solutions displayed only the charge transfer

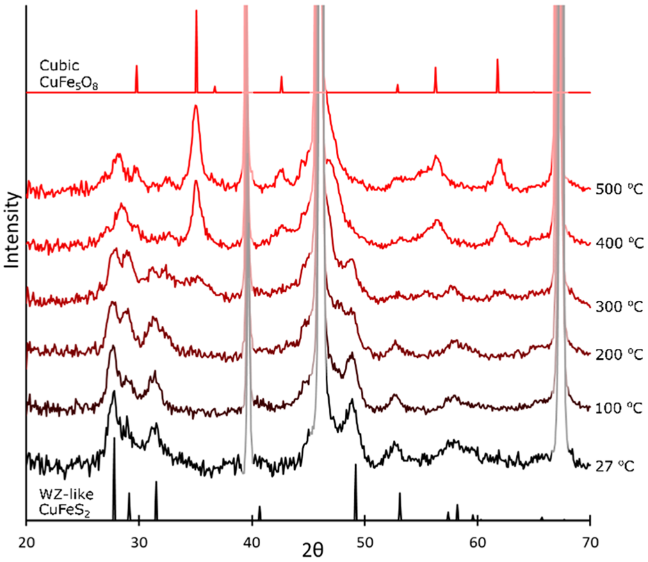

Figure 5. Temperature-dependent pXRD of WZ-like $CuFeS_2$ NCs. Reflections by the platinum sample holder signals at approximately 39, 47, and 67° 2θ have been faded.

bands and yellow color of typical $FeCl_3$ 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).[44] 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 catalyzes 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 transiton.[18,45] A corollary observation has been made by Steimle et al. who noticed that phosphines can induce lattice sulfur vacancies that catalyze the transformation of $Cu_{1.8}S$ 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 $CuFeS_2$.[46]

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.[2,47] However, if the conversion process is event driven and kinetically determined, one would expect that individual particles express either WZ or CP phase but not both; under these intermediate conditions, not all particles experience the event that catalyzes the transformation from hexagonal to 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 equiv to 1 equiv (to iron), the product diffraction pattern resembled what would be expected if the weaker donating $P(p\text{-}C_6H_4Cl)_3$ was 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-versus L-type ligands were needed to influence phase between cubic and hexagonal structures. The previous work suggests a thermodynamic stabilization of ligand surfaces influences phase. Here, the effect is kinetic. We hypothesize the ligands affect 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 and 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 the 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

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.nanolett.0c03122.

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 phosphorus ligands; further HRTEM of $CuFeS_2$ products (PDF)

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All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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