Synthetic studies of colloidal nanoparticles that crystallize in metastable structures represent an emerging area of interest in the development of novel functional materials, as metastable nanomaterials may exhibit unique properties when compared to their counterparts that crystallize in thermodynamically preferred structures. Herein, we demonstrate how phase control of colloidal AgInSe$_2$ nanocrystals can be achieved by performing reactions in the presence, or absence, of 1-dodecanethiol. The thiol plays a crucial role in formation of metastable AgInSe$_2$ nanocrystals, as it mediates an in-situ topotactic cation exchange from an orthorhombic Ag$_2$Se intermediate to a metastable orthorhombic phase of AgInSe$_2$. We provide a detailed mechanistic description of this cation exchange process to structurally elucidate how the orthorhombic phase of AgInSe$_2$ forms. Density functional theory calculations suggest that the metastable orthorhombic phase of AgInSe$_2$ is metastable by a small margin, at 10 meV/atom above the thermodynamic ground state. In the absence of 1-dodecanethiol, a mixture of Ag$_2$Se nanocrystal intermediates form that convert through kinetically slow, non-topotactic exchange processes to yield the thermodynamically preferred chalcopyrite structure of AgInSe$_2$. Finally, we offer new insight into the prediction of novel metastable multinary nanocrystal phases that do not exist on bulk phase diagrams.
Ligand-Mediated Phase Control in Colloidal AgInSe$_2$ Nanocrystals

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ABSTRACT: Synthetic studies of colloidal nanoparticles that crystallize in metastable structures represent an emerging area of interest in the development of novel functional materials, as metastable nanomaterials may exhibit unique properties when compared to their counterparts that crystallize in thermodynamically preferred structures. Herein, we demonstrate how phase control of colloidal AgInSe$_2$ nanocrystals can be achieved by performing reactions in the presence, or absence, of 1-dodecanethiol. The thiol plays a crucial role in formation of metastable AgInSe$_2$ nanocrystals, as it mediates an in-situ topotactic cation exchange from an orthorhombic Ag$_x$Se$_{1-x}$ intermediate to a metastable orthorhombic phase of AgInSe$_2$. We provide a detailed mechanistic description of this cation exchange process to structurally elucidate how the orthorhombic phase of AgInSe$_2$ forms. Density functional theory calculations suggest that the metastable orthorhombic phase of AgInSe$_2$ is metastable by a small margin, at 10 meV/atom above the thermodynamic ground state. In the absence of 1-dodecanethiol, a mixture of Ag$_x$Se nanocrystal intermediates form that convert through kinetically slow, non-topotactic exchange processes to yield the thermodynamically preferred chalcopyrite structure of AgInSe$_2$. Finally, we offer new insight into the prediction of novel metastable multinary nanocrystal phases that do not exist on bulk phase diagrams.

KEYWORDS: silver indium selenide • chalcopyrite • nanocrystals • metastability • cation exchange • dodecanethiol

Metastability, broadly defined, is the kinetic persistence of a system that exists in a higher free energy state than the thermodynamically most stable state for a given set of conditions. The application of metastable materials are ubiquitous, and include examples from diamond wafers for semiconductor applications to the use of technetium-99m as a radiotracer in gamma ray imaging.$^{1,2}$ All nanomaterials are inherently metastable with respect to their bulk material counterparts as a result of their high surface energies and large surface area-to-volume ratios.$^{3,4}$

In addition to the useful properties afforded by size effects for colloidal nanocrystal analogs of thermodynamically stable bulk materials of that same crystal phase, the thermodynamic scales of phase equilibria on the nanoscale are often compressed, allowing relatively low-temperature syntheses of crystalline polymorphs that only exist at much higher temperatures and/or pressures in the bulk.$^{5-8}$ Furthermore, entirely new crystal phases can arise on the nanoscale that have no known counterparts in bulk.$^{9-13}$ Because the physical properties of a material are linked to its crystalline structure, the ability to isolate new or difficult-to-access metastable structures on the nanoscale holds promise for the discovery of novel functional materials with properties different from, and possibly superior to, the properties of more thermodynamically stable materials.$^{14-18}$ To synthetically target such materials, it is important to consider that a metastable state is only isolable if, under some set of conditions, that state represents a thermodynamic minimum.$^5$ In other words, if a state is never the thermodynamically most stable state under any set of conditions, it is not synthetically accessible.

The synthetic chemistry of colloidal nanocrystals that persist in metastable states with respect to their bulk analogs remains a science largely dependent on empirical findings, rather than on bottom-up design principles. This is partially a result of the myriad variables that can contribute to phase determination, such as nanocrystal size,$^9$ surface area-to-volume ratio,$^{19}$ surface functionalization,$^{14}$ crystal defects,$^9$ etc. These confounding variables make it difficult to draw direct analogies between the thermodynamic phase diagrams of bulk materials and corresponding stabilities at the nanoscale,$^{20-22}$ thus making the predictable syntheses of metastable colloidal nanocrystals an outstanding challenge.$^{23}$

Diorganyl dichalcogenides (R-E-E-R, where E = S, Se, Te, and R = Ph, Me, Bz, etc.) are proven molecular precursors for the preparation of colloidal metal chalcogenide nanocrystals, and in particular, for the preparation of metastable phases of these nanocrystals, including wurtzite or wurtzite-like phases of CuInS$_2$, Cu$_2$SnSe$_3$, Cu$_2$ZnSnS$_4$, and Cu$_2$S.$^{24-27}$ We were the first to report a previously unknown wurtzite-like phase of CuInS$_2$ from a synthesis utilizing a diselenide precursor, which was shown to be critical in phase determination of the resulting nanocrystals. We subsequently determined that the functional groups on the diselenide precursor could be leveraged to molecularly program different polymorphs of the resulting colloidal CuInS$_2$ nanocrystals depending on the C–Se precursor bond strength.$^{28}$ Herein, we explore a related ternary chalcogenide, AgInS$_2$, that is of interest for applications in near-infrared luminescence and as a solar absorber for thin film photovoltaics.$^{30-34}$ Like CuInS$_2$, AgInS$_2$ belongs to the family of I-III–V$_2$ semiconductors that adopt a thermodynamically preferred chalcopyrite structure in bulk. Possessing an A$^+$B$^{2-}$E$^{-2}$ composition, the diamondoid structure of chalcopyrite can be thought of as a supercell of zinc blende, where the A$^+$ and B$^{2-}$ cations are ordered in the cation sub-lattice and the Se$^{2-}$ sub-lattice adopts a cubic close packed structure. In the case of AgInS$_2$, a metastable orthorhombic phase is also known to exist only on the nanoscale, where the Se$^{2-}$ sub-lattice adopts a hexagonally close-packed structure. Isostuctural with the high-temperature orthorhombic phase of bulk AgInS$_2$, the In$^{3+}$ and Ag$^+$ cations in this metastable phase of AgInS$_2$ are ordered and alternate along the [001] crystallographic direction.$^{34}$

While dichalcogenides have been utilized to access a wide range of metastable colloidal nanocrystal phases, as previously mentioned, it has also been observed that the presence or absence of coordinating ligands influences phase determination in these reactions.$^{14,35-37}$ Herein, we elucidate the role of a coordinating ligand in the phase determination of AgInS$_2$ nanocrystals synthesized using dibenzyl diselenide as the selenium precursor. This mechanism
is notably different from previously proposed mechanisms for the formation of metastable orthorhombic AgInSe₂ nanocrystals. Finally, we propose a general conceptual framework that explains the isolation of previously empirically discovered metastable poly-crystalline materials.

RESULTS AND DISCUSSION

In a typical reaction, AgNO₃ and In(OAc)₃ were dissolved together in a mixture of 1-octadecene (ODE), 1-dodecanethiol (DDT), and oleic acid. In a separate flask, the dibenzyl diselenide (Bn₂Se₂) selenium source was dissolved in DDT and ODE. The metal precursor solution was then heated and the solution containing the diselenide was hot injected into the metal precursors at 200 °C. Under these reaction conditions, we observed the formation of colloidal AgInSe₂ nanocrystals that crystallize in the orthorhombic Pna₂₁ space group, which is a metastable phase of AgInSe₂ known to form only on the nanoscale (Figure 1). The powder X-ray diffraction (XRD) pattern of the phase-pure orthorhombic nanocrystals is given in Figure 1a. Rietveld refinement of the XRD pattern using the Pna₂₁ space group returns lattice parameters of a = 7.315(2), b = 8.536(3), and c = 6.963(3) Å, with a unit cell volume of V = 434.8(1) Å³. These values are in close agreement with the previously reported experimental values for orthorhombic AgInSe₂ (i.e., a = 7.33 Å, b = 8.52 Å, and c = 7.02 Å; V = 438 Å³). This orthorhombic phase is similar to the wurtzite structure type, with the notable distinction between them being the ordering of Ag⁺ and In³⁺ in the orthorhombic structure. Discerning wurtzite from wurtzite-like structures can be difficult and has been a point of interest within studies of metastable ternary chalcogenide materials. In this case, orthorhombic AgInSe₂ space group exhibits distinct low-angle reflections (at 15-16° 2θ) from the (110) and (011) lattice plane families, which are absent in a higher symmetry wurtzite structure type (space group P6₃mc, see Figure S1). The Rietveld refinement and the observation of low-angle reflections in Figure S1 leads us to conclude that the metastable AgInSe₂ nanocrystals do indeed assume a wurtzite-like structure that maintains Ag⁺ and In³⁺ ordering within the crystalline lattice.

The diselenide precursor is important for phase determination. When substituting Bn₂Se₂ for grey selenium in the same solvent mixture, the reaction does not yield product due to the low solubility and reactivity of Se powder under these reaction conditions. However, when Se powder is dissolved in oleylamine and used as the selenium source under otherwise similar conditions, the reaction gives chalcopyrite AgInSe₂ nanocrystals. Nonetheless, formation of the metastable orthorhombic phase of AgInSe₂ using Bn₂Se₂ was a surprising result, as it differs from what we observed when employing Bn₂Se₂ in the synthesis of CuInSe₂ nanocrystals; there, diselenide precursors possessing relatively weak C-Se bonds, including Bn₂Se₂, gave the thermodynamically preferred chalcopyrite phase of CuInSe₂. Thus, we anticipated that Bn₂Se₂ might similarly produce the thermodynamically preferred chalcopyrite phase of AgInSe₂, yet this turned out not to be the case. This indicates that the mechanism of formation of this metastable phase when using Bn₂Se₂ is distinct from that which was previously observed for the formation of CuInSe₂.

Althougn Bn₂Se₂ leads to the metastable orthorhombic phase of AgInSe₂, we surmised that increasing the reaction temperature might yield the thermodynamic phase of AgInSe₂. The initial reactions with Bn₂Se₂ to give orthorhombic AgInSe₂ nanocrystals were performed at 220 °C. Increasing reaction temperatures to 250 °C still resulted in formation of metastable orthorhombic AgInSe₂ with no indication of chalcopyrite formation by XRD (Figure 1a). Annealing powders of the metastable AgInSe₂ nanocrystals to 300 °C in the solid state also does not cause the material to thermally relax to the chalcopyrite phase, even after several heating/cooling cycles (Figures S2, S3). Moreover, after leaving the as-prepared orthorhombic AgInSe₂ nanocrystals for ~10 months on the lab bench under ambient conditions, they maintain their metastable orthorhombic structure (Figure S2). Heating the as-synthesized orthorhombic AgInSe₂ nanocrystals at 300 °C for 1 h as a colloidal suspension in ODE also leaves the metastable phase mostly intact, although some conversion to the chalcopyrite phase was observed, indicating that this metastable phase is more resistant to relaxation as a powder at high temperatures than as a colloid in solution (Figure S2). Empirically, the orthorhombic phase of these AgInSe₂ nanocrystals appears to be a local minimum in the energetic landscape of this material system that has a high barrier to reorganization to the thermodynamically preferred phase, and thus the orthorhombic phase remains kinetically frozen.

To explore the potential roles of the coordinating species (i.e., DDT and oleic acid) in phase determination, they were systematically omitted from the reactions. When oleic acid is omitted from the reaction by replacing it with an equal volume of DDT, under otherwise identical conditions, the reaction still returns orthorhombic AgInSe₂ (Figure S4). This suggests that oleic acid does not play...
a major role in phase determination. Conversely, when DDT is replaced by an equal volume of oleic acid, we found that the analogous hot-injection reaction with Bn$_2$Se$_2$ performed at 250 °C yields chalcopyrite AgInSe$_2$ with minor Ag$_2$Se impurities (Figure S4). This result illustrates that: (1) Bn$_2$Se$_2$ can give the thermodynamic phase under certain reaction conditions, and (2) DDT plays a critical role in phase determination in this reaction.

**Formation of Chalcopyrite AgInSe$_2$** To probe the formation of chalcopyrite AgInSe$_2$, a study was performed without DDT in which aliquots were removed at certain time points after the injection of Bn$_2$Se$_2$. Powder XRD patterns of nanocrystal products isolated from each aliquot show a complex mixture of Ag$_2$Se intermediates at early times that, over the span of 15 min, convert into chalcopyrite AgInSe$_2$ upon reaction with In$^{3+}$ in solution (Figure 2a). Bulk Ag$_2$Se exhibits two stable polymorphs — namely, a low-temperature orthorhombic phase and a high temperature ($T > 130$ °C) cubic phase. However, an additional metastable tetragonal polymorph is known to form within polycrystalline thin films and for Ag$_2$Se nanocrystals. To the best of our knowledge, the crystal structure of this tetragonal phase of Ag$_2$Se has not yet been unambiguously determined, in large part due to its instability as a bulk material under any known conditions. Even so, Wang et al. conducted a thorough investigation of the phase transitions that occur between the tetragonal, orthorhombic, and cubic phases of Ag$_2$Se nanocrystals by variable-temperature powder XRD measurements. For their system, they reported that the tetragonal phase undergoes a phase transition to the cubic phase at ~110 °C, whereas the low-temperature orthorhombic phase converts to the cubic phase at ~140 °C.

Figure 2a illustrates that 1 min after injecting Bn$_2$Se$_2$ into the metal precursor solution in the absence of DDT, all three distinct polymorphs of Ag$_2$Se are present (i.e., orthorhombic, tetragonal, and cubic structures). Phase quantification of each respective polymorph is difficult due to the high degree of overlap of the powder XRD patterns of these three phases. Both the orthorhombic and the tetragonal phases of Ag$_2$Se are likely metastable at the reaction temperature of the aliquot study, and they are both capable of undergoing direct phase transitions to form cubic Ag$_2$Se at elevated temperatures, which led us to believe that perhaps the cubic phase of Ag$_2$Se is the binary intermediate that ultimately gives rise to chalcopyrite AgInSe$_2$. However, a control experiment in which Bn$_2$Se$_2$ was hot-injected into a flask containing only AgNO$_3$ (i.e., with no In(OAc)$_2$ precursor) revealed that these Ag$_2$Se phases do not undergo phase transitions to the cubic phase of Ag$_2$Se after 30 min (Figure S5) under the same conditions used for the aliquot study shown in Figure 2a, suggesting that each of the intermediate Ag$_2$Se phases must be capable of directly converting to chalcopyrite AgInSe$_2$ in the presence of In$^{3+}$ cations. This observation is supported by the fact that on the bulk Ag$_2$Se-In$_2$Se$_3$ pseudo-binary phase diagram of AgInSe$_2$, both cubic and orthorhombic Ag$_2$Se can convert to chalcopyrite AgInSe$_2$ with increasing In$^{3+}$ content. On the nanoscale, conversion of Ag$_2$Se to AgInSe$_2$ can be thought of as a partial cation exchange in which two equivalents of Ag$_2$Se combine with one equivalent of In$^{3+}$ to yield AgInSe$_2$ with the expulsion of three Ag$^+$ ions. Neither orthorhombic nor cubic Ag$_2$Se have cubic close-packed Se$^{2-}$ anion sub-lattices (i.e, cubic Ag$_2$Se is body-centered cubic and orthorhombic Ag$_2$Se is nearly hexagonally close-packed, vide infra), whereas the Se$^{2-}$ sub-lattice of chalcopyrite AgInSe$_2$ is cubic close-packed (see Figure S6). Thus, to generate chalcopyrite AgInSe$_2$ nanocrystals from Ag$_2$Se intermediates, a reconstructive transition via non-topotactic cation exchange must occur in which the Se$^{2-}$ sub-lattice reorganizes to a cubic close-packed structure.

While this reorganization to the chalcopyrite structure is thermodynamically favored, it is necessarily kinetically slow. For that reason, the hot-injection syntheses without DDT always resulted in products comprised of chalcopyrite AgInSe$_2$ with some binary Ag$_2$Se impurities, even when reactions were carried out in the presence of excess In(OAc)$_3$ and for extended periods of time (Figure S7). To improve the phase purity of the chalcopyrite AgInSe$_2$ products, a heating up procedure can be employed, whereby all reagents were combined in a flask with oleic acid and ODE and heated to the desired reaction temperature. This method proved to be more effective in converting the Ag$_2$Se intermediates to a product containing almost exclusively chalcopyrite AgInSe$_2$ (Figure S7).
Formation of Orthorhombic AgInSe₂ and the Role of DDT. The formation of orthorhombic AgInSe₂ nanocrystals in the presence of DDT suggests that DDT changes the mechanism of formation for the ternary material. To better understand the mechanism of formation of orthorhombic AgInSe₂ nanocrystals when DDT is present, we performed additional aliquot studies with a hot-injection of the Bn₂Se₂ as the selenium precursor. In contrast to the long-lived binary Ag₅Se intermediate observed in the aliquot study with no DDT (Figure 2a), the analogous aliquot study in the presence of DDT reveals fast conversion of precursors to the metastable orthorhombic AgInSe₂ product (Figure 2b). The amount of DDT was reduced from the 20 equivalents (relative to the metal precursors) used in the original synthesis to 5 equivalents in order to better observe any binary Ag₅Se intermediates (Figure 2c).

Above this threshold value, conversion happened so quickly that no binary intermediates were observed preceding the formation of orthorhombic AgInSe₂. Notably, Figure 2c illustrates how when DDT is present, the predominate intermediate observed is the orthorhombic phase of Ag₅Se, and not the complex mixture of silver selenides that was observed in the absence of DDT, indicating that orthorhombic Ag₅Se is the intermediate that leads to orthorhombic AgInSe₂. This fast conversion of orthorhombic Ag₅Se elucidates the role of DDT in the reaction; as a soft base, it is capable of mediating cation exchange from the orthorhombic Ag₅Se phase that is otherwise kinetically sluggish to react in the presence of soft In³⁺ cations due to the low intrinsic ionic conductivity of orthorhombic Ag₅Se (~10⁻³ S/cm). While others have observed the presence of orthorhombic Ag₅Se prior to the formation of orthorhombic AgInSe₂, this transformation is not well understood in the literature. Abazović et al. speculated that the formation of the metastable phase of AgInSe₂ is in some way related to how ligands bind to the surfaces of the ternary nanocrystal nuclei, thus directing the phase towards orthorhombic AgInSe₂. We propose a more nuanced mechanism of formation for orthorhombic AgInSe₂ whereby a DDT-mediated topotactic cation exchange converts orthorhombic Ag₅Se to orthorhombic AgInSe₂.

Structural comparisons of orthorhombic Ag₅Se to orthorhombic AgInSe₂ reveal similarities between these two crystal structures and elucidate how the process of cation exchange transforms the former into the latter. Upon examining the Se²⁻ sub-lattice of orthorhombic Ag₅Se, it is apparent that there exists a nearly hexagonally close-packed network of Se²⁻ anions in the [010] direction (Figure 3a). These hexagonal sheets of Se²⁻ are nearly planar, although the in-plane Se-Se angles are distorted from the 120° in-plane angles within the hexagonal lattice of orthorhombic AgInSe₂ (Figure 3a, b). The interplanar d-spacing between Se²⁻ sheets along the [010] direction in orthorhombic Ag₅Se is 3.56 Å, whereas the d-spacing along the [001] direction of close packing in AgInSe₂ is slightly less, at 3.51 Å. Moreover, the average Se-Se distance within a hexagonal sheet of Se is 4.53 Å for orthorhombic Ag₅Se and 4.24 Å for orthorhombic AgInSe₂. Topotactic cation exchange from orthorhombic Ag₅Se to orthorhombic AgInSe₂ should naturally allow for this slight lattice contraction, considering the ionic radius of four-coordinate Ag⁺ is 1.29 Å and that of four-coordinate In³⁺ is 1.94 Å. Overall, the Se²⁻ sub-lattice of orthorhombic Ag₅Se resembles that of AgInSe₂, since only slight changes are needed to take the former to the latter.

Considering that the Se²⁻ sub-lattices are so similar, the redistribution of cations upon cation exchange with In³⁺ comprises a more significant structural transformation in going from orthorhombic Ag₅Se to orthorhombic AgInSe₂. The asymmetric unit of orthorhombic Ag₅Se has one crystallographically unique Se²⁻ site and two unique Ag⁺ sites. Of the two Ag⁺ sites, one site resides within a tetrahedral hole. These tetrahedra share edges with two adjacent, symmetrically equivalent tetrahedra along the [100] direction. The other Ag⁺ site exists in a trigonal planar coordination geometry (Figure 3d).
The orthorhombic structure of AgInSe₂ is a wurtzite-like structure in that the Se²⁻ sub-lattice is hexagonally close-packed and all cations reside in corner-sharing tetrahedral coordination environments. Thus, to form this structure from orthorhombic Ag₂Se, cation exchange needs to occur in a manner that disrupts the edge-sharing and trigonal planar coordination geometries to yield the requisite corner-sharing tetrahedron motif. To achieve such a transformation, the periodic tetrahedral holes that exist within the structure of orthorhombic Ag₂Se (Figure 3c, e) need to be filled by either incoming In³⁺ ions or by neighboring Ag⁺ ions that, when migrating, would then leave corner-sharing tetrahedral holes that In³⁺ could fill. Figure 3e demonstrates how removing the edge-sharing tetrahedra and trigonal planar coordination environments from the orthorhombic Ag₂Se structure, and placing cations within the periodic tetrahedral holes, leads to the wurtzite-like structure of orthorhombic AgInSe₂. Occupation of the tetrahedral holes in orthorhombic AgInSe₂ would lead to unstable, edge-sharing configurations with both the proximal Ag⁺ tetrahedra and trigonal planar sites (Figure 3c). Every In³⁺ ion incorporated into the structure necessarily must expel three Ag⁺ ions to maintain charge neutrality. Therefore, it is useful to visualize a transformation wherein each In³⁺ atom displaces one Ag⁺ atom from a neighboring tetrahedral coordination site and two Ag⁺ atoms from trigonal planar coordination sites, creating more stable corner-sharing configurations via the displacement of edge-sharing motifs within the structure. While the mechanism described above illustrates how the corner-sharing network of tetrahedra in orthorhombic AgInSe₂ can be derived from orthorhombic Ag₂Se, it does not explicitly explain how or why the specific ordering of cations in orthorhombic AgInSe₂ arises through this transformation. In fact, the tetrahedral holes within orthorhombic Ag₂Se are periodic such that along the [001] direction, they form a linear channel of vacancies (Figure 4a). If all In³⁺ cations were to occupy these vacancies, the resulting ternary structure would contain linear chains of Ag⁺ and In³⁺ in the [001] direction, where the cations within each chain would be identical (Figure 4d). However, this arrangement of cations is not present within the orthorhombic structure of AgInSe₂, rather, the cationic sites along the [010] direction alternate between Ag⁺ and In³⁺ (Figure 4b). This indicates that an ion hopping process is operative during cation exchange such that Ag⁺ ions migrate to accommodate incoming In³⁺. By comparing the calculated electrostatic site potentials and Madelung energy of the orthorhombic AgInSe₂ structure to the site potentials and Madelung energy of the structure that would result by simply filling the periodic holes within orthorhombic Ag₂Se, we find that there is an electrostatic driving force that causes this shuffling of Ag⁺ during cation exchange; in the theoretical ternary structure, derived directly from orthorhombic Ag₂Se with no ion hopping, the calculated In³⁺ site potential is greater (1.54 e/Å) than that for the In³⁺ site in orthorhombic AgInSe₂ (-1.67 e/Å), which is an indication that electrostatic repulsion between neighboring In³⁺ ions is more significant in this theoretical arrangement than in the orthorhombic structure of AgInSe₂. This finding is also supported by the Madelung energy calculations, which represents the attractive electrostatic component to the lattice energy of an ionic solid. The Madelung energy of the theoretical ternary structure is higher in energy (-7.38 MJ/mol) than that of the experimentally observed orthorhombic AgInSe₂ structure (-7.60 MJ/mol; see SI for calculation details).

The Materials Project database contains thermodynamic information calculated on six polymorphs on AgInSe₂, two of which are experimentally known (I4̅2d, R3m), and four of which are theoretical structures (R3m, I4̅/amd, Fdd2, P6/mmm) calculated by DFT. Of these, the tetragonal I4̅2d polymorph is predicted to be stable, with the trigonal R3m polymorph exhibiting a degree of metastability at 0.1 eV/atom above the 0 K convex hull (Figure S8). Typically, materials with a predicted metastability in the range of 0.1 eV/atom are considered in principle synthesizable under appropriate conditions, although this is highly dependent on chemical composition. To supplement these calculations, an additional calculation was performed on the orthorhombic Pna_2₁ polymorph of AgInSe₂. The Pna_2₁ polymorph was found to have a formation energy of 0.412 eV/atom, which is 10 meV/atom above the predicted stable chalcopyrite phase of AgInSe₂. Figure S8 combines this result with existing Materials Project data calculated using the phase diagram analysis capability of the pymatgen package. This low lying metastability is not unprecedented; in fact, many metastable metal selenide materials are less than 25 meV/atom above the thermodynamic ground state, and the median energy above the ground state for metastable ternary polymorphs irrespective of composition is 6.9 meV/atom. Thus, while the orthorhombic structure is metastable, it is only higher in energy than the chalcopyrite structure by a small margin, which may explain why it is isolable.

**Predicting the Syntheses of Novel Metastable Polymorphs on the Nanoscale.** Predictable syntheses of metastable materials at large remain a challenge. From this work, and our previous work on phase control of CuInSe₂ nanocrystals, we note an interesting pattern emerging. In both cases, the metastable ternary chalcogenide nanocrystals form via cation exchange from low-temperature structures of binary selenides, which are metastable at the relatively high temperatures of their respective nanocrystal syntheses.
lead to ternary materials, is insightful and can act as a guide when material systems, and the phase diagrams of the binaries that could intermix anionic structures by reacting with a third element in such a way that the ternary anionic system that exhibits sub-
ternary structures. (b) Reaction scheme explaining isolation of metastable ternary silver selenides, the low-temperature (CuInSe$_2$ and orthorhombic Ag$_2$Se) and high-temperature (Cu$_2$Se and cubic Ag$_2$Se) phases differ significantly in their Se$^2-$ sub-lattices, with the low-temperature phases of each being pseudo-hexagonal and the high-temperature phases assuming face-centered and body-centered cubic Se$^2-$ sub-lattices, respectively. As mentioned above, the chalcopyrite structure type possesses a face-centered cubic Se$^2-$ sub-lattice. Therefore, isolating metastable ternaries in these cases relies on the conversion of binary selenides that possess Se$^2-$ sub-lattices that do not form in bulk for the ternary materials. In the formation of both metastable polymorphs of AgInSe$_2$ and CuInSe$_2$, kinetically fast topotactic cation exchange mechanisms provide the means of preserving the distinct hexagonal Se$^2-$ sub-lattices upon reaction within In$^{3+}$. These mechanisms out-compete processes that would otherwise lead to the thermodynamically preferred crystal structures, and instead lead to metastable ternary structures that do not exist on their respective bulk phase diagrams for the ternary selenides.

More generally, a promising area to explore in the rational discovery of new metastable nanomaterials may be within material systems that exhibit sub-lattice mismatches between the binary and ternary anionic sub-lattices, where the binary polymorphs with distinct anionic sub-lattices could generate new metastable ternary structures by reacting with a third element in such a way that the anionic sub-lattice is preserved. In effect, lattice mismatches between anionic sub-lattices can act as effective kinetic barriers that restrict quick access to thermodynamic structures, allowing for the isolation of metastable polymorphs on the nanoscale, exemplified by Figure 5. Inspecting pseudo-binary phase diagrams for ternary material systems, and the phase diagrams of the binaries that could lead to ternary materials, is insightful and can act as a guide when searching for lattice mismatches to exploit for new metastable nanomaterial syntheses.

To check that this conceptual framework holds true for more than just CuInSe$_2$ and AgInSe$_2$, we inspected the pseudo-binary phase diagram of the Cu$_2$Se-SnSe$_2$ system; here, with increasing Sn$^4+$ content, cubic Cu$_2$Se (66.7 % Cu, 33.3 % Se, stable above $\sim$130 °C) converts to a cubic, sphalerite phase of Cu$_2$SnSe$_2$. However, the low-temperature Cu$_2$Se$_2$ phase (60 % Cu, 40 % Se) has a pseudo-hexagonal anionic sub-lattice and it maintains a Cu:Se ratio within the boundaries of the two-phase Cu$_2$Se-SnSe$_2$ region. Therefore, we expect a kinetically fast reaction of Cu$_2$Se$_2$ with Sn$^4+$ to produce a metastable, hexagonal phase of Cu$_2$SnSe$_2$ since there exists a sub-lattice mismatch in going from Cu$_2$Se$_2$ to the thermodynamically preferred sphalerite phase of Cu$_2$SnSe$_2$. Indeed, such a metastable hexagonal phase exists that was previously unknown in bulk, as we first reported the isolation of wurtzite-like Cu$_2$SnSe$_2$ nanocrystals in 2012. This further illustrates the utility of leveraging sub-lattice mismatches to generate novel metastable materials.

We hypothesize that this conceptual framework can also be extended to the predictable isolation of metastable phases not present on bulk phase diagrams for quaternary materials. To support this hypothesis, we turned to the Cu$_2$ZnSnS$_4$ literature. Cu$_2$ZnSnS$_4$ is a quaternary material that possesses a face-centered cubic anionic sub-lattice and crystalizes with a kesterite structure type, analogous to the diamondoid chalcopyrite structure type for ternary materials. The quasi-ternary Cu$_2$S-ZnS-Sn$_2$$_3$ phase diagram shows that, in bulk, the introduction of Zn$_2$S and Sn$_2$$_3$ into Cu$_2$S results in the conversion of a Cu$_2$S polymorph (digenite, a high-temperature phase stable up to 1130 °C) with a face-centered cubic anionic sub-lattice to kesterite Cu$_2$ZnSnS$_4$. However, wurtzite-like Cu$_2$ZnSnS$_4$ nanocrystals have been synthesized, despite the fact that this phase does not exist in bulk. Phenomenologically, this wurtzite-like phase must be the result of kinetically fast reactions with a low-temperature phase of Cu$_2$ZnS (such as djurelite or roxbyite) that does not possess an fcc anionic sub-lattice. Thus, the predictive power of this conceptual framework can be proven by using it to explain empirically discovered metastable ternary and quaternary nanomaterials. In summary, coupling the identification of material systems that exhibit lattice mismatches between potential kinetic intermediates and the thermodynamically expected products with computations that reveal the energetics of the predicted metastable phases could provide a useful new methodology for the rational discovery of metastable nanomaterials that have never been observed before on bulk phase diagrams.

CONCLUSIONS

In conclusion, this work sheds light on the mechanism of phase determination in AgInSe$_2$ nanocrystals. More specifically, DDT mediates a fast cation exchange from orthorhombic Ag$_2$Se to form a metastable phase of orthorhombic AgInSe$_2$. Without the use of DDT as an exchange mediator, this orthorhombic Ag$_2$Se intermediate cannot undergo cation exchange due to its low intrinsic ionic mobility. For reactions that occur in the absence of DDT, various silver selenide intermediates form and then convert to the thermodynamic chalcopyrite structure of AgInSe$_2$ via kinetically slow non-topotactic cation exchange processes. In addition to elucidating the mechanism for formation of the metastable orthorhombic phase of AgInSe$_2$, we discovered that its isolation likely also correlates with the fact that it is only marginally metastable at 10 meV/atom above the ground state. Finally, we provide a new conceptual framework to predict metastable polymorphs that do not form in bulk; using phase diagrams, it is possible to identify sub-lattice mismatches that exist between kinetic intermediates that form quickly in nanocrystal syntheses and the thermodynamically most stable polymorphs for multinary materials. Fast conversion of
intermediates with distinct sub-lattices can generate new metastable structures of multinary nanomaterials not present on bulk phase diagrams. In predicting these new phases, convex hull calculations can provide an idea of whether or not such metastable materials should be isolable from a thermodynamic perspective.

**EXPERIMENTAL SECTION**

**Materials and General Procedures.** Silver(I) nitrate (AgNO₃, Alfa Aesar, 99.9%), indium(III) acetate (In(OAc)₃, Alfa Aesar, 99.9%), dibenzyl diselenide (Bn₂Se₂, Alfa Aesar, 95%), 1-dodecanethiol (DDT, Alfa Aesar, 98%), 1-octadecene (ODE, Sigma-Aldrich, 90%), oleic acid (Alfa Aesar, 90%), and selenium powder ~200 mesh (Alfa Aesar, 99.999%) were all used as received, with no further purification. All solvents were degassed prior to use for 4 h at 105 °C and then overnight at room temperature. Reactions were conducted under a nitrogen atmosphere using standard Schlenk techniques. All reactions employed J-KEM temperature controllers with in-situ thermocouples in order to control and monitor the temperature of the reaction vessel.

**Synthesis of AgInSe₂ Nanocrystals.** We adapted the general synthesis of AgInSe₂ nanocrystals from Deng et al., but here using a diselenide precursor. In a typical synthesis, AgNO₃ (16.9 mg, 0.1 mmol) and In(OAc)₃ (29.1 mg, 0.1 mmol) were loaded into a 25 mL three-neck round-bottom flask. Bn₂Se₂ (34.0 mg, 0.1 mmol) was added to a separate two-neck round-bottom flask. In the syntheses of orthorhombic AgInSe₂ nanocrystals, 4 mL of ODE, 0.5 mL of DDT, and 50 μL of oleic acid were added to the three-neck flask and 0.5 mL of ODE and 0.5 mL of DDT were added to the two-neck flask. In the syntheses of chalcophyrte AgInSe₂ nanocrystals, all DDT was replaced with an equal volume of oleic acid, keeping the volumes of ODE constant. After adding the solvents, the flasks were degassed at 100 °C for 1 h. The metal precursor-containing flask was then ramped to 250 °C at 10 °C/min under nitrogen. Upon reaching a high temperature (200 °C for DDT-containing reactions and 230 °C for reactions not containing DDT), the Bn₂Se₂ solution was injected into the metal precursor-containing flask, resulting in nucleation of nanocrystals (the relatively low 200 °C injection temperature for DDT-containing reactions was implemented to prevent formation of sulfides prior to injection of the diselenide). Following injection, the three-neck flask recovered upon heating to a total of 30 min after injection. The three-neck flask was then quenched by placing it in a room temperature water bath. The crude product was then split into two 40 mL centrifuge tubes and filled to volume with ethanol. The centrifuge tubes were bath sonicated for 10 min, and centrifuged for 3 min. The product was redispersed in 5 mL of hexane in each centrifuge tube and filled to volume with ethanol. This washing procedure was repeated two more times to yield particles for XRD analysis.

**Aliquot Studies.** All aliquot studies were performed using the same experimental protocols described for the synthesis of AgInSe₂ nanocrystals; however, to capture the various intermediates that precede AgInSe₂ formation, the final reaction temperatures (and amount of DDT in the case of orthorhombic AgInSe₂) were reduced from 250 °C for the initial syntheses to 230 °C. In the case of orthorhombic AgInSe₂, this reduction in temperature was still not enough to capture the timescale of formation of the ternary phase. To observe the binary orthorhombic Ag₂Se intermediate, the amount of DDT for the aliquot study was reduced to 20 equivalents with respect to the metal precursors to 5 equivalents. Under these conditions, we were able to observe the binary intermediate.

**Characterization.** Powder X-ray diffraction (XRD) measurements were performed on a Rigaku Ultima IV powder X-ray diffractometer using Cu Kα radiation (λ = 1.5406 Å). Samples were analyzed on a zero-diffraction silicon substrate. Transmission electron microscopy (TEM) micrographs were obtained from dropcast samples supported on holey carbon-coated copper TEM grids (Ted Pella, Inc.). Grids were placed in a vacuum oven overnight at 60 °C for removal of volatile organics. A JEOL JEM-2100 microscope with a Gatan Orius charge-coupled device (CCD) camera was used to take TEM images at an operating voltage of 200 kV. Thermogravimetric analysis (TGA) was performed on a TGA Q50 instrument with a heating rate of 10 °C/min with an approximate sample size of 10 mg in an alumina crucible.

**Density Functional Theory (DFT).** Formation energy calculations were performed on the orthorhombic Pna₂₁ polytype using the Vienna Ab-initio Simulation Package (VASP), plane-augmented wave pseudopotentials and a k-point density of 64 points per Å³, consistent with Materials Project standard settings to ensure the energies would be directly comparable to existing Materials Project calculations. The atomic positions and crystal lattice were allowed to relax, resulting in lattice parameters of a = 7.48 Å, b = 8.76 Å and c = 7.14 Å. These calculations were performed using the PBE exchange-correlation functional, and so lattice parameters are expected to be slightly over-estimated compared to experiment.

**ASSOCIATED CONTENT**

**Supporting Information**

The Supporting Information is available free of charge on the ACS Publications website.

Additional figures including simulated and experimental XRD patterns; TGA traces; control aliquot studies; Se₂⁺ sub-lattice illustrations; Rietveld refinements and parameters; Madelung constant and site potential calculation details (PDF)

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**Notes**

The authors declare no competing financial interest.

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Supporting Information

Ligand-Mediated Phase Control in AgInSe$_2$ Nanocrystals

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Figure S1. Simulated powder XRD patterns of AgInSe$_2$ in the (a) $Pna_{2}1$ space group and in the (b) wurtzite $P6_3mc$ space group. Note that the $Pna_{2}1$ structure can be distinguished by unique reflections at 15-16° 2θ from the (110) and (011) lattice plane families, which are absent in a higher symmetry wurtzite structure type. The inset illustrates an experimental powder XRD pattern of the as-synthesized orthorhombic AgInSe$_2$ nanocrystals; the minor reflections at 15-16° 2θ are observed, confirming that these nanocrystals crystallize in the $Pna_{2}1$ space group.

Figure S2. (a) Annealing powders of the as-prepared orthorhombic AgInSe$_2$ nanocrystals to 300 °C does not cause the material to thermally relax to the thermodynamically preferred chalcopyrite structure by XRD, even after several heating-cooling cycles, indicating that there is a barrier to a phase transition to the chalcopyrite phase. Note, however, that at these temperatures some of the Ag$^+$ is reduced to Ag. Powder XRD of the material taken from the TGA crucible after heating to 450 °C shows that the reduction of Ag$^+$ to Ag is more pronounced at higher temperatures, but that the orthorhombic phase also still persists. Notably, this progression of XRD patterns was taken from a material that had been left on the lab bench for 10 months. (b) Heating as-synthesized orthorhombic AgInSe$_2$ nanocrystals in 1-octadecene at 300 °C for 1 h shows that the orthorhombic phase is still predominant, although XRD indicates some conversion of orthorhombic to chalcopyrite AgInSe$_2$. 
Figure S3. (a) TGA trace of orthorhombic AgInSe₂ up to 300 °C; the material shows minimal mass loss at this temperature. (b) TGA trace of orthorhombic AgInSe₂ up to 450 °C; here, a much larger mass loss is evident, as the surface ligands are stripped from the nanocrystal surface at this temperature. It is possible that ligand loss from the nanocrystal surface correlates with the observed reduction of Ag⁺ to Ag shown in Figure S2.

Figure S4. (a) Powder XRD pattern of orthorhombic AgInSe₂ that forms when only DDT and ODE are included in the reaction, indicating that oleic acid is not important in the isolation of the metastable phase. (b) When DDT is replaced by an equal amount of oleic acid in the solvent mixture, chalcopyrite AgInSe₂ forms with some Ag₂Se impurities by powder XRD, indicating DDT is important in phase determination.
Figure S5. Powder XRD aliquot studies of a reaction in which Bn$_2$Se$_2$ was hot-injected into a flask containing a solution of only AgNO$_3$ (with no In(OAc)$_3$ present). A complex mixture of Ag$_2$Se polymorphs results. Although cubic Ag$_2$Se is the thermodynamically stable polymorph at the reaction temperatures, no significant phase transitions were observed over the time scale of the reaction, indicating that the other phases of Ag$_2$Se present are kinetically resistant towards a phase transition to cubic Ag$_2$Se under these conditions.

Figure S6. (a) Se$^{2-}$ sub-lattice of chalcopyrite AgInSe$_2$; note that the lattice is fcc as it contains an ABC packing motif. (b) Se$^{2-}$ sub-lattice of cubic Ag$_2$Se; this lattice is body-centered cubic.
Figure S7. Hot-injection reactions (highlighted with yellow background) that were allowed to react for longer times in the presence of excess In$^{3+}$ (the initial reactions were performed with 1:1 In:Ag ratios) did not produce phase-pure AgInSe$_2$ by power XRD. Heating-up reactions (highlighted with blue background) showed better conversion to chalcopyrite AgInSe$_2$ in the presence of excess In$^{3+}$, with the 3 h reaction producing nearly phase-pure chalcopyrite AgInSe$_2$ as shown by a Rietveld refinement of powder XRD data in (b). All heating-up reactions were performed at 250 °C.

Figure S8. (a) The 0 K phase diagram of the Ag-In-Se chemical system, color coded by calculated formation energy. (b) The relative ordering of AgInSe$_2$ polymorphs, as predicted by calculation.

Electrostatic site potential and Madelung energy calculations:

The orthorhombic AgInSe$_2$ CIF served as a template to create the CIF of the theoretical structure that would result if the vacancies in the orthorhombic Ag$_2$Se structure were directly filled by In$^{3+}$ (we derived the CIF of orthorhombic AgInSe$_2$ itself from a CIF of the isostructural AgInS$_2$, corrected for lattice parameters, unit cell volume and composition. The collection code for the AgInS$_2$ CIF in the ICSD is 51618). Because the space group of this theoretical structure was not known, the space group was defined as P1 in the CIF and the Cartesian coordinates of each atom in the structure were explicitly defined.

The VESTA software allows users to calculate electrostatic site potentials and Madelung energies based on user inputs. For all calculations, user inputs for radius = 1 Å and for region = 4 Å$^{-1}$. The output for Madelung energy calculations is in terms of energy per mole of asymmetric units; because the CIF of the theoretical structure explicitly defined the coordinates of each atom without the use of symmetry operators, the asymmetric unit was the entire unit cell. The unit cell is formally Ag$_4$In$_4$Se$_8$, so to get the Madelung energy on a per mole basis, the final output was divided by four.
Rietveld refinement results:

Rietveld refinements were performed in GSAS. Refinement results for the orthorhombic phase of AgInSe$_2$:

| Lattice parameters | Fractional coordinates | Multiplicity | Occupancy | $U_{iso}$ |
|--------------------|------------------------|--------------|-----------|-----------|
| $a$ (Å) 7.315101   | Atom                   | $x$          | $y$       | $z$       | 4          | 1.0000     | 0.06123    |
| $b$ (Å) 8.536572   | Ag1                    | 0.394398     | 0.116473  | 0.147136  | 4          | 1.0000     | 0.02835    |
| $c$ (Å) 6.963848   | In1                    | 0.065165     | 0.119095  | 0.624407  | 4          | 1.0000     | 0.06927    |
| $\alpha$ (°) 90.0000 | Se1                  | 0.115775     | 0.645775  | 0.003793  | 4          | 1.0000     | 0.02992    |
| $\beta$ (°) 90.0000 | Se2                  | 0.093749     | 0.075877  | 0.982046  | 4          | 1.0000     | 0.02835    |
| $\gamma$ (°) 90.0000 |                    |             |           |           |            |            |            |

Goodness of Fit Parameters

| $\chi^2$ | Texture Index | Space Group |
|----------|---------------|-------------|
| 1.963    | 1.6233        | Pna2$_1$    |

References:

1. Momma, K.; Izumi, F.; VESTA: a Three-Dimensional Visualization System for Electronic and Structural Analysis, *VESTA Manual* 2019.
