

Coloring Tetrahedral Semiconductors: Synthesis and Photoluminescence Enhancement of Ternary II-III₂-VI₄ Colloidal Nanocrystals

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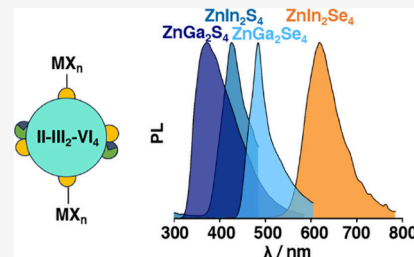


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Supporting Information

ABSTRACT: Ternary tetrahedral II-III₂-VI₄ semiconductors, where II is Zn or Cd, III In or Ga, and VI S, Se, or Te, are of interest in UV radiation detectors in medicine and space physics as well as CO₂ photoreduction under visible light. We synthesize colloidal II-III₂-VI₄ semiconductor nanocrystals from readily available precursors and ascertain their ternary nature by structural and spectroscopic methods, including ⁷⁷Se solid-state NMR spectroscopy. The pyramidally shaped nanocrystals range between 2 and 12 nm and exhibit optical gaps of 2–3.9 eV. In the presence of excess anions on the particle surface, treatment with Lewis acidic, Z-type ligands results in better passivation and enhanced photoluminescence. Electronic structure calculations reveal the most stable, lowest energy polymorphs and coloring patterns. This work will pave the way toward more environmentally friendly, ternary semiconductors for optoelectronics and electrocatalysis.



Tetrahedral semiconductors are indispensable materials in both established and emerging technologies ranging from advanced computing and telecommunications to biophotonics and renewable energy.^{1–3} For example, doped diamond finds use in various electrochemical sensors and high-power electronics, whereas silicon plays a crucial role in transistors, computer chips, and solar cells.^{4,5} CdTe, GaN, GaAs, and other tetrahedral binary semiconductors are useful in lasers, solar cells, detectors, nanoinks, tunneling diodes, and imaging applications.^{6,7} At the nanoscale, the chemistry of unary (elemental) and binary tetrahedral semiconductors continues to advance at a rapid pace.⁸ Doped systems and solid solutions such as In_xGa_{1-x}As, Hg_{1-x}Cd_xTe, and atomically precise ternaries such as CuInS₂ are of growing interest because of their infrared activity.^{9–11} Other tetrahedral ternary semiconductors with band gaps in the visible region provide additional opportunities for fundamental research and technological development.^{12,13}

Ternary tetrahedral semiconductors with the general formula II-III₂-VI₄, where II is Zn or Cd, III a group 13 element (“triel” or Tr) like In or Ga, and VI a chalcogen (Ch) such as S, Se, or Te, have rich crystallography and a wide array of optoelectronic properties (Figure 1a). With band gaps in the ~2–4 eV range, II-III₂-VI₄ semiconductors exhibit birefringence, nonlinear susceptibility, and intense photoluminescence.^{14,15} Their photosensitivity makes them useful in UV

radiation detectors for medicine and space physics.¹⁶ ZnGa₂Se₄, ZnGa₂Te₄, and CdGa₂Te₄ could also be efficient catalysts.^{17,18} A computational screening based on optical cross sections ($\epsilon > 3.6 \times 10^4 \text{ cm}^{-1} \text{ eV}$), exciton binding energies (<200 meV), and absorption anisotropies (>0.8) predicted CO₂ activity comparable to that of anatase TiO₂, but under visible light.¹⁷ Some II-III₂-VI₄ compositions are less toxic alternatives to more commonly used semiconductors.

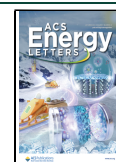
Built from corner sharing [IICh₄]⁶⁻ and [TrCh₄]⁵⁻ tetrahedra, II-III₂-VI₄ semiconductors adopt a chalcopyrite-type structure with an ordered cation vacancy arrangement.¹⁹ Among multiple polymorphs, space groups $\bar{I}42d$ and $F\bar{4}3m$ prevail at higher temperatures.²⁰ ZnGa₂S₄ crystallizes in three tetragonal polymorphs ($\bar{I}42m$, $P\bar{4}2m$, and $\bar{I}4$),²¹ whereas ZnGa₂Se₄ has one cubic ($F\bar{4}3m$) and two tetragonal structures ($\bar{I}42m$ and $\bar{I}4$), see below and Supporting Information (SI). ZnIn₂S₄ has one cubic ($Fd\bar{3}mS$), two trigonal ($P\bar{3}m1$, $R3mH$),

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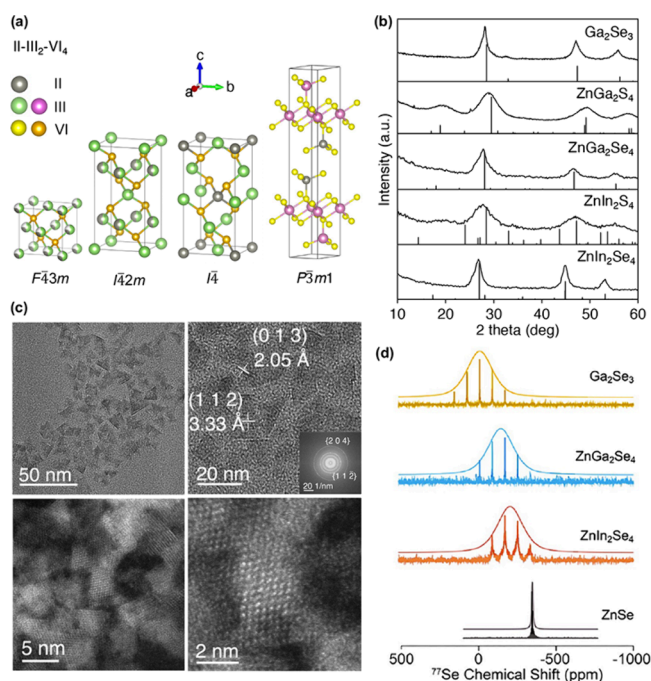


Figure 1. (a) Unit cells of select II-III₂-VI₄ polymorphs. (b) Powder XRD of ZnGa₂S₄, ZnGa₂Se₄, ZnIn₂S₄, ZnIn₂Se₄, and Ga₂Se₃ nanocrystals and standards (ICSD-44886, ICSD-44887, ICSD-15637, ICSD-25647, and ICSD-76754, respectively). (c) Representative bright-field, fast Fourier transform (FFT), and dark-field TEM of 8.2 ± 3.8 nm ZnIn₂Se₄. (d) Experimentally measured direct excitation ⁷⁷Se CPMG SSNMR spectra of Ga₂Se₃, ZnGa₂Se₄, and ZnIn₂Se₄ nanocrystals, acquired with a MAS frequency of 25 kHz, a CPMG pulse sequence, 75 s recycle delay, and averaging 1024 scans; 9.4 T magnetic field. Peak fits overlaid on experimental CPMG NMR.

and one hexagonal polymorph (*P*₆*3**mc*), whereas ZnIn₂Se₄ has three with mixed-Zn/Ga cation sites.

High temperature solid-state reactions using the elements,^{22,23} or between the lower order binaries,²⁴ result in poly- (bulk) or single-crystal versions of II-III₂-VI₄ materials. Molecular beam epitaxy and chemical bath deposition produce thin films of ZnGa₂Se₄ and ZnIn₂Se₄.²⁵ Solvothermal methods generate ZnIn₂S₄ microspheres,^{26,27} as well as II/III/VI frameworks that resemble Sn- and S-doped versions of ZnGa₂Se₄.²⁸ A few syntheses^{29–31} generate nanoscale versions of ZnGa₂S₄, ZnGa₂Se₄, and ZnIn₂S₄. Colloidal II-III₂-VI₄ nanocrystals remain underexplored.

Here we present a widely applicable and reproducible route to prepare ternary II-III₂-VI₄ nanocrystals. This method generates stable colloidal solutions of monodisperse (2–12 nm) particles of ZnGa₂S₄, ZnGa₂Se₄, ZnIn₂S₄, and ZnIn₂Se₄ from commercially available precursors. We characterize the nanocrystals using X-ray diffraction, UV–visible absorption, photoluminescence (PL), electrochemistry, and solid-state NMR spectroscopy. While routine powder XRD fails to distinguish their binary impurities, SSNMR confirms the identity and purity of the ternary II-III₂-VI₄ nanophases. The photoluminescence of the nanocrystals can be enhanced by treatment with Lewis acids (Z-type ligands). Electronic structure calculations unveil the relative energies of their different polymorphs and coloring patterns.

Injection of bis(trimethylsilyl)sulfide (TMS₂S) or diphenyl diselenide (PhSeSePh) into a mixture of Zn(OAc)₂·2H₂O and

Scheme 1. Solution-Phase Synthesis and Metal-Halide Treatment of Colloidal II-III₂-VI₄ and III₂VI₃ Nanocrystals.

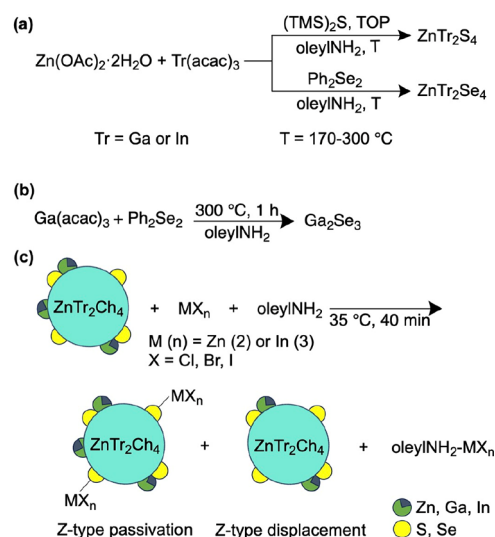


Table 1. Synthesis of Colloidal II-III₂-VI₄ Nanocrystals^a

precursors ^a			T (°C)	product(s) (Scherrer, TEM/nm)
Zn(II) 0.1 mM	Tr(III) 0.2 mM	Ch(VI) 0.4 mM		
OAc	Ga(acac) ₃	(TMS) ₂ S	300	ZnGa ₂ S ₄ (2.3 ± 0.1)
OAc	Ga(acac) ₃	Ph ₂ Se ₂	290	ZnGa ₂ Se ₄ (4.7 ± 0.4)
OAc	In(acac) ₃	(TMS) ₂ S	170	ZnIn ₂ S ₄ (3.3 ± 1.6)
OAc	In(acac) ₃	Ph ₂ Se ₂	270	ZnIn ₂ Se ₄ (5.6 ± 0.1, 8.2 ± 3.8)
OAc	Ga(acac) ₃	Ph ₂ Se ₂	300	Ga ₂ Se ₃ (6.7 ± 0.5)

^a6 mL oleylNH₂ + TOP; 1 h; St = stearate.

Tr(acac)₃ (Tr = Ga, In) in oleylamine at 100 °C, followed by heating to 170–300 °C, results in colloidal II-III₂-VI₄ nanocrystals (Scheme 1). Powder X-ray diffraction (XRD) of solids isolated from this reaction are consistent with the standard patterns reported for *I*₄ ZnGa₂S₄, *I*₄ ZnGa₂Se₄, *P*₆*3**mc* ZnIn₂S₄, and *I*₄ ZnIn₂Se₄ (Figure 1b). Line width analysis reveals Scherrer dimensions between 2.3–5.6 nm (Table 1, see SI). Bright- and dark-field transmission electron microscopy (TEM) show uniform pyramidal morphologies. *d* Spacing from fast Fourier transform (FFT) measurements are consistent with the powder XRD data (Figure 1c). Energy dispersive X-ray spectroscopy (EDS) under the scanning electron microscope (SEM) yields the compositions: Zn_{0.8}Ga_{2.0}S_{4.7}, Zn_{1.1}Ga_{2.0}Se_{2.7}, Zn_{0.9}In_{2.0}S_{3.9}, and Zn_{1.0}In_{2.0}Se_{3.9}, in good agreement with the theoretical formulas. TEM-EDS analysis confirms all three elements are colocalized.

Unlike unary or binary nanocrystal synthesis, where precursor decomposition generates monomer units that coalesce into larger particles with the same composition as the final product, ternary (and other multinary) nanocrystal evolution involves multiple phases in a stepwise fashion.^{32,33} For example, nucleation of Bi seeds precedes formation of colloidal NaBiS₂ and NaBiSe₂ nanocrystals.³² Nucleation of metallic Zn seeds, followed by heterogeneous deposition of a Pn shell, precede formation of LiZnSb nanocrystals.³⁴ Successful synthesis of multinary colloids requires mild precursors and conditions capable of producing sufficiently small, reactive seeds that live long enough to proceed to these

additional heterogeneous nucleation, interfacial reaction, and phase transformation steps.

Reactions between long-chain zinc carboxylates, triel chlorides, and selenourea produce, instead of ternaries, mixtures of ZnSe and SeO_x . Unlike hydrolysis-prone triel chlorides, triel-acetylacetonates are less reactive.³⁵ In addition, PhSeSePh contains a relatively weak Se–Se bond (43.63 kcal mol^{−1}) and two stronger C(Ph)–Se bonds (64.4 kcal mol^{−1}), both of which must break to release [Se].^{36–38} We hypothesize that PhSe· radicals, generated by facile homolysis of the weaker Se–Se bond, suppress runaway growth of Zn-, Ga-, or In-based seeds. Interestingly, the metal–organic chalcogenolate In-(SePh)₃ precedes ternary ZnIn₂Se₄ (SI).^{39,40} At higher temperatures (≥ 200 °C), this intermediate then reacts with the [Se] released from *in situ* cleavage of the C–Se bonds in PhSeSePh to yield ZnIn₂Se₄ nanocrystals (Table 1).³⁶

In the case of the sulfur-derived nanocrystals, the metal acetate or oleylamine complex formed *in situ* may react with TMS₂S to form binary seeds (ZnS, Tr₂S₃),⁴¹ which subsequently evolve into ternary nanocrystals. The synthesis of chalcopyrite nanocrystals follows a similar phase evolution.⁴² While our approach provides a synthetic entry into phase-pure ternary nanocrystals, otherwise parasitic side reactions can be put to good use. For example, reaction between Ga(acac)₃ and Ph₂Se₂ at 300 °C produces freestanding, colloidal *F*43m Ga₂Se₃ nanocrystals. Only substrate-bound versions of these were reported.^{43,44} Scherrer analysis of XRD peak widths yields an average size of 6.7 ± 0.5 nm, with a slightly Se-rich EDX composition of Ga_{2.0}Se_{3.6}.

The standard XRD patterns of ternary II-III₂-VI₄ and binary III₂VI₃ materials are very similar (Figure 1b), making unambiguous confirmation of ternary composition difficult based on powder XRD alone. While EDX area scans and colocalization data above are consistent with a near-stoichiometric ternary composition, we sought an additional technique that would unequivocally probe the structure of the nanocrystals at the atomic level. Solid-state (SS)NMR spectroscopy measures the chemical shift of NMR active nuclei based on the local environment of the different chemical sites, thus enabling the determination of the true speciation of a sample.⁴⁵ Thus, we resorted to ⁷⁷Se SSNMR spectroscopy to conclusively ascertain the ternary structure and distinguish ZnGa₂Se₄ and ZnIn₂Se₄ from Ga₂Se₃ and ZnSe.

The lowest energy polymorph of ZnGa₂Se₄ and ZnIn₂Se₄, *I*4, (see below) possesses one ⁷⁷Se coordination environment: SeZnTr₂. To enhance the sensitivity of ⁷⁷Se SSNMR experiments, we used a Carr–Purcell Meiboom–Gill (CPMG) pulse sequence.^{46–48} Each of ZnGa₂Se₄ and ZnIn₂Se₄ exhibits unique, inhomogeneously broadened ⁷⁷Se peaks (Figure 1d), in agreement with other nanocrystals.^{49–51} This broadening reflects the small particle size, which creates a distribution of surface, near-surface, and interior (bulk-like) Se sites. By coupling of spin ¹/₂ ⁷⁷Se nuclei to the abundant quadrupolar nuclei, ⁶⁹/₇₁Ga or ¹¹⁵In could also cause inhomogeneous broadening. Critically, ⁷⁷Se SSNMR spectra of binary Ga₂Se₃ and ZnSe exhibit different chemical shifts. Crystalline β-Ga₂Se₃ features Se atoms that bind to two- or three-Ga atoms with approximate chemical shifts of 190 ppm and 0 ppm, respectively.⁵² Because the distribution of ⁷⁷Se chemical shifts exceeds the chemical shift differences, we observe a single broad peak for Ga₂Se₃. The ⁷⁷Se SSNMR spectra of synthesized and commercial ZnSe are much narrower than those of Ga₂Se₃ or ternary nanocrystals.

The light absorption onsets of ternary nanocrystals are between 2.0–3.9 eV (Figure 2a). This is consistent with band

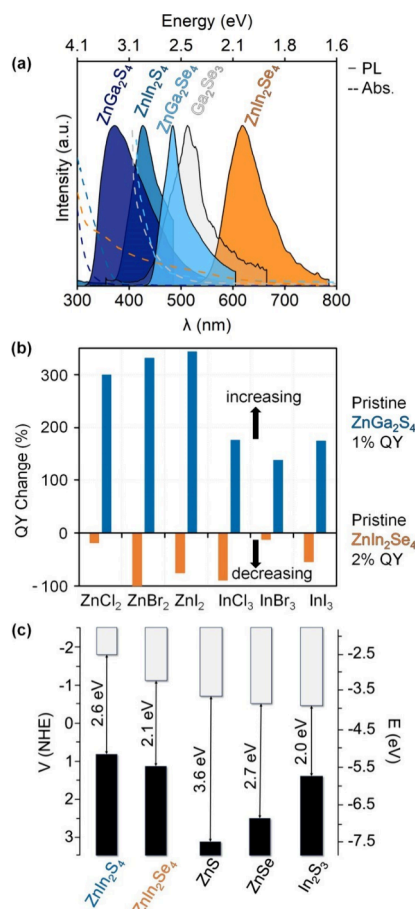


Figure 2. (a) Optical absorption and photoluminescence, (b) effect of Z-type (Lewis acidic) ligands on PL QY, and (c) electrochemically determined energies of II-III₂-VI₄ nanocrystals (bulk ZnS, ZnSe, and In₂S₃ included for reference).

gap values derived from extrapolation of the linear region of direct $(\text{Abs} \cdot h\nu)^2$ vs $(h\nu)$ Tauc plots (Table 2 and SI). The

Table 2. Band Gaps of II-III₂-VI₄ and III₂VI₃ Nanocrystals.

composition	band gap energy (eV)				
	experimental			theoretical	
	abs	echem	lit	VASP	LMTO
ZnGa ₂ Se ₄	3.9	nd ^a	3.3	2.3	2.3
ZnGa ₂ Se ₄	2.7	nd ^a	2.4	1.2	1.2
ZnIn ₂ Se ₄	3.2	2.6	2.3		
ZnIn ₂ Se ₄	2.1	2.1	2.2		
Ga ₂ Se ₃	2.0	nd ^a	2.1		
ZnSe	2.7	nd ^a	2.7	1.7	1.1

^aNot determined.

values are in agreement with previous literature reports from single crystals and thin films.^{23–26} The absorption onset and optical gap of Ga₂Se₃ nanocrystals are also consistent with single crystals⁴⁴ and are distinct from its ternary counterpart, ZnGa₂Se₄. Among ternaries, there is an inverse relationship between band gap value and isotropic ⁷⁷Se chemical shift. The optical band gap widens with increasing electronegativity of the

triol or lattice parameter, a (SI). A similar relationship exists for I–III–Ch₂ materials.⁵³

Cyclic voltammograms (CVs) on glassy carbon electrodes display well-defined first oxidation and reduction waves under an inert atmosphere corresponding to the anodic and cathodic peak potentials as well as the oxidation and reduction onsets (SI). Different scan rates result in the same electrochemical peaks. The electrochemically measured ionization potentials (IP) and electron affinities (EA) for ZnIn₂S₄, ZnIn₂Se₄, and select binaries corroborate the band gap values obtained from optical absorption (Figure 2c).

All ternary II–III₂–VI₄ nanocrystals display band edge photoluminescence (PL), with quantum yields (QYs) between 0.1–2.2% (Figure 2a). Postsynthetic modification with X-, L-, or Z-type ligands can minimize surface defects by passivating undercoordinated atoms or dangling bonds,^{54–56} which act as surface traps and lower QYs via nonradiative recombination.^{57,58} Interestingly, the effect of this treatment is highly dependent on particle stoichiometry: MX₂ (Z-type) treatment (M = Zn, In; X = Cl, Br, I) of sulfur-rich Zn_{0.8}Ga_{2.0}S_{4.7} leads to a two- to four-fold enhancement in PL QY (+140–340%, see SI), whereas that of selenium-poor Zn_{1.0}In_{2.0}Se_{3.9} decreases it significantly (–20–100%, Figure 2b). We hypothesize that MX₂-induced PL enhancement in II–III₂–VI₄ nanocrystals with anion-rich surfaces is due to Z-type passivation, while reduced PL in those with anion-deficient surfaces is due to Z-type displacement of surface cations (Scheme 1c). Similar QY increases were observed for II–VI and III–V QDs.⁵⁷

To gain deeper insight into precise structure and atom ordering, we conducted *ab initio* calculations on ZnGa₂S₄ and ZnGa₂Se₄. Beyond electronic structures of II–III₂–VI₄ materials,^{21,59} a comprehensive study of mixed site occupancies, superstructures or “coloring” patterns, is lacking.^{32,60,61} Because the $\bar{I}42m$ polymorph of ZnGa₂S₄ features mixed cation sites (Figure 1), we considered three possible superstructures: $\bar{I}42m$ S1, $\bar{I}42m$ S2, $\bar{I}42m$ S3 (SI). We constructed three superstructures for each of the two ($\bar{I}42m$ and $F43m$), out of three, polymorphs of ZnGa₂Se₄ with mixed cation sites. The XRD patterns of the supercells fail to distinguish the experimental patterns, thus we utilized the Vienna *ab initio* simulation package (VASP)⁶² to calculate the relative energies. Using the Perdew–Burke–Ernzerhof (PBE) functional, we relaxed the cell parameters prior to computing relative energies. Our results suggest that $\bar{I}4$ is the lowest energy polymorph for ZnGa₂S₄ and ZnGa₂Se₄, while the cubic and $\bar{I}42m$ S1 phases remain close in energy (Figure 3). Other superstructures are ~ 2.8 – 3.2 eV/ f_u less stable, likely due to the presence of short Ch–Ch contacts, as compared to the sum of the van der Waals radii,⁶³ resulting in destabilizing lone-pair and electrostatic cation–cation repulsions.⁶⁴

Band structure and density of states (DOS) calculations using the linear muffin-tin orbital (LMTO) model with the all-electron, quasi-relativistic tight-binding LMTO program and the Atomic Spheres Approximation⁶⁵ show the lowest energy ($\bar{I}4$) polymorphs of ZnGa₂S₄ and ZnGa₂Se₄ have direct gaps, with values of 1.37 and 2.25 eV, respectively (Figure 3b,c, and SI). These underestimate the experimental values by ca. 30–40%, a common feature of LDA calculations (for example, II–III₂–VI₄²¹ and I–V–VI₂).³² Similar band structure calculations on ZnSe were used to validate our results. While VASP is slightly better than LMTO, both underestimate the well-known “bulk” ZnSe band gap of 2.70 eV by a comparable amount (Figure 3d,e and Table 2). Thus, the experimental band gaps of the

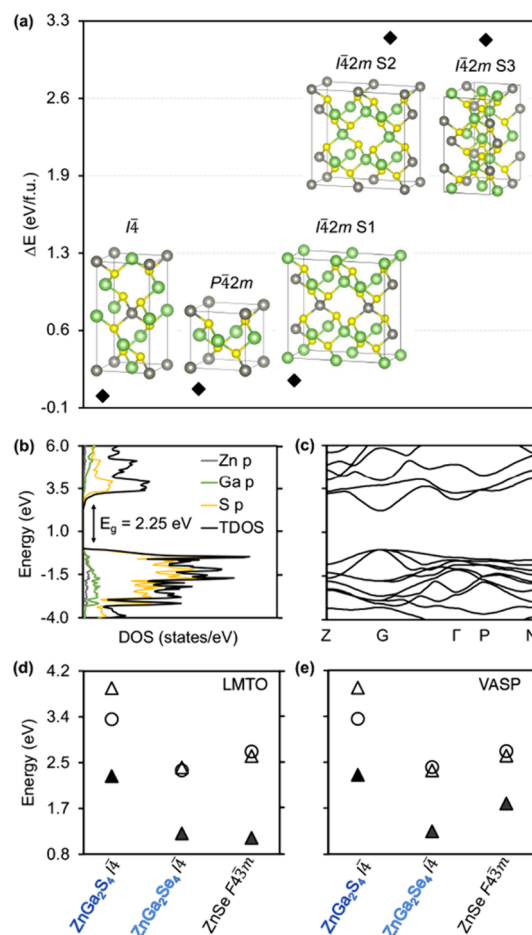


Figure 3. (a) Relative energies of ZnGa₂S₄ polymorphs. (b) Density of states, and (c) band structure of $\bar{I}4$ ZnGa₂S₄. Theoretical ($\blacktriangle$), (d,e) experimental ($\triangle$), and literature (O) band gaps of lowest energy tetragonal ($\bar{I}4$) ZnGa₂Se₄ and ZnGa₂S₄ (zinc blende ZnSe added as reference).

ternary nanocrystals align best with those calculated for the $\bar{I}4$ polymorphs.

In summary, we developed a highly reproducible colloidal synthesis of emissive ternary II–III₂–VI₄ nanocrystals. A combination of structural, analytical, electrochemical, and spectroscopic methods, including ⁷⁷Se SSNMR, corroborates their ternary nature, homogeneity, and phase purity. Treatment with Lewis acidic Z-type ligands passivates chalcogen-rich nanocrystal surfaces, increasing the PL; in contrast, a similar treatment causes Z-type displacement of cations from anion-deficient surfaces, decreasing the PL. Electronic structure calculations identify lowest energy phases, shedding light on the experimental vs theoretical band gaps of II–III₂–VI₄ materials. Future efforts will aim at testing the photo- and electrocatalytic activity of these materials.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <http://pubs.acs.org/doi/10.1021/acsenenergylett.4c02032>.

XRD, EM, QY, and SSNMR data, coloring and electronic structure calculations (PDF)

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Notes

The authors declare no competing financial interest.

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