Size-Driven Stability of Lanthanide Thiophosphates Grown from an Iodide Flux

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Supporting Information

ABSTRACT: To determine the influence of the lanthanide size on the structures and properties of thiophosphates, a thiophosphate series containing different lanthanides was synthesized via high temperature flux crystal growth and their structures and physical properties analyzed and compared. Layered thiophosphates NaLnP$_2$S$_6$ (Ln = La, Ce, Pr) and thiopyrophosphates CsLnP$_2$S$_6$ (Ln = Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er, Yb, Y) were grown out of an iodide flux using consistent reaction conditions across both series. Under the mildly reducing iodide flux reaction conditions, a rather rare example of phosphorus reduction from the +5 to the +4 oxidation state was observed. Both resultant structure types are based on lanthanide thiophosphate sheets with the alkali cations located between them. Magnetic susceptibility measurements were conducted and revealed Curie–Weiss behavior of the samples, with a Van Vleck contribution in the CsSmP$_2$S$_6$ sample. UV–vis data was found to be in good agreement with the literature, indicating little influence of the sulfide environment on the localized 4f orbitals.

INTRODUCTION

The pervasive interest in main group, transition, and rare earth metal sulﬁde chemistry is driven by their structural diversity and unique properties. Replacing hard Lewis base oxide ligands with soft sulﬁdes leads to a change in the bonding between the metal center and the ligand resulting in changes in the optical, magnetic, and structural properties of the materials. Recently, particular interest has been directed toward thiophosphate materials that exhibit conducting and applications, and, as a result, have generated signiﬁcant interest. There have been only ﬁve lanthanide thiopyrophosphates reported to date, KErP$_2$S$_6$ KSmP$_2$S$_6$ and TlLnP$_2$S$_6$ (Ln = Ce, Pr, Nd). Conventional, uranium metal and sulfur have been used to produce uranium(IV) in a reaction mixture. A direct reaction between them requires a slow heating step that signiﬁcantly slows down exploratory crystal growth. To eliminate this step, uranium(IV) sulﬁde was utilized as a convenient uranium source. The same applies to the lanthanide sulﬁde materials, the syntheses of which have often involved lanthanide metals and elemental sulfur as a starting material. In this report, we focus on the synthesis and properties of the rare-earth thiopyrophosphates with the

in the crystal lattice for extended periods of time. The majority of known thiophosphates are composed of either the simplest thiophosphate unit, P(V)S$_4^{−}$, or hexathiopyrophosphate, P(IV)$_2$S$_6^{4−}$ anions. The thiopyrophosphate and hexathiometaphosphate compounds are far less studied, and their properties are yet to be revealed.

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Table 1. Crystallographic Data for NaLaP$_6$, NaCeP$_6$, and CsLnP$_7$ (Ln = Y, Pr, Nd, Sm)

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general formula CsLnP$_7$, Ln = Pr, Nd, Sm, Gd–Er, Yb, synthesized using lanthanide sulfides LnS$_3$ as the rare earth metal starting material. Despite employing the identical reaction conditions, there is a clear dependence of the products on the size of the lanthanide cation. All samples were obtained in a phase-pure form and characterized using single crystal X-ray diffraction, UV–vis spectroscopy, and magnetic susceptibility measurements.

### EXPERIMENTAL SECTION

#### Materials.
P$_5$S$_2$ (99%, Sigma-Aldrich), CdI$_2$ (99.9%, Alfa Aesar), NaI (99.9%, Alfa Aesar), Na$_2$S (Alfa Aesar), La$_2$O$_3$ (Alfa Aesar, 99.99%), CeO$_2$ (Alfa Aesar, 99.99%), Pr$_2$O$_3$ (Alfa Aesar, 99.99%), Nd$_2$O$_3$ (Alfa Aesar, 99.99%), Sm$_2$O$_3$ (Alfa Aesar, 99.99%), Gd$_2$O$_3$ (Alfa Aesar, 99.9%), Ho$_2$O$_3$ (Alfa Aesar, 99.99%), Er$_2$O$_3$ (Alfa Aesar, 99.99%), and Yb$_2$O$_3$ (Alfa Aesar, 99.99%) were used as received. P$_5$S$_2$ and Na$_2$S were stored and handled in a nitrogen glovebox. Rare earth sulfides were obtained according to the procedure described in the literature (see SI for a detailed description of the procedure).

#### Synthesis.
NaLaP$_6$, NaCeP$_6$, and CsLnP$_7$ (Ln = Pr–Sm, Gd–Er, Yb) were all obtained under the same synthetic conditions. A fused silica tube was charged with 0.16 mmol of a rare earth sulfide, 0.96 mmol of Na$_2$S, 1.28 mmol of P$_5$S$_2$ (1:6:8 molar ratio), and 0.5 g of CdS–NaI eutectic flux (obtained by melting 3.0 g of CdS and NaI in 20 h, after which the furnace was cooled to room temperature by switching it off). The products were isolated by removing the flux...
with DMF, filtered, and dried in air. The yields (based on the lanthanides) are 15% (La), 10% (Ce), 29% (Pr), 29% (Nd), 24% (Sm), 27% (Gd), 42% (Tb), 30% (Dy), 53% (Ho), 55% (Er), and 69% (Yb). Several similar reactions with Tm,S,

as a starting material were attempted; however, no product was obtained in any of them. Experiments with different dwelling times were performed using the same heating and cooling profiles in the same furnace to ensure the reproducibility of the results. A reaction with 0.50 g of CsCl/NaCl eutectic flux was carried out using the same reaction conditions except for the dwell temperature, which was set to 550 °C to ensure melting of the flux.

**Single Crystal X-ray Diffraction.** Single-crystal X-ray diffraction data were collected at 300(2) K on a Bruker D8 QUEST diffractometer equipped with an Incoatec IgS 3.0 microfocus radiation source (MoKα, λ = 0.71073 Å) and a PHOTON II area detector. The crystals were mounted on a microloop using immersion oil. The raw data reduction and absorption corrections were performed using SAINT and SADABS programs. Initial structure solutions were obtained with SHELXS-2017 using direct methods and Olex2 GUI. Full-matrix least-squares refinements against F² were performed with SHELXL software. All the structures were checked for missing symmetry with the Addsym program implemented into PLATON software and no higher symmetry was found. The crystallographic data and results of the diffraction experiments are summarized in Tables 1 and 2.

**Powder X-ray Diffraction.** Powder X-ray diffraction (PXRD) data for phase purity confirmation were collected on polycrystalline samples ground from single crystals (Figures S2–S11). Data were collected on a Bruker D2 PHASER diffractometer using Cu Kα radiation over a 2θ range 10–65° with a step size of 0.02°.

**Energy-Dispersive Spectroscopy (EDS).** EDS was performed on single crystal products using a Tescan Vega-3 SEM equipped with a Thermo EDS attachment. The SEM was operated in low-vacuum mode. Crystals were mounted on an SEM stub with carbon tape and analyzed using a 20 kV accelerating voltage and an 80 s accumulation time. The results of EDS confirm the presence of elements found by single-crystal X-ray diffraction (Figure S12 and Table S1).

**Optical Properties.** UV–vis spectra were recorded using a PerkinElmer Lambda 35 UV/Visible scanning spectrophotometer used in the diffuse reflectance mode and equipped with an integrating sphere (Figures S13–S24). Diffuse reflectance spectra were recorded in the 200–900 nm range. Reflectance data were converted to absorbance using the Kubelka–Munk function.

**Magnetism.** Magnetic property measurements were performed using a Quantum Design MPMS 3 SQUID magnetometer. Zero-field-cooled (ZFC) magnetic susceptibility measurements were performed from 2 to 300 K in an applied magnetic field of 0.1 T. The raw data were corrected for radial offset and sample shape effects according to the method described in the literature.

**Crystal Chemical Calculations.** Crystal structure analysis was performed using the TOPOS 4.0 software package. The method of intersecting spheres was employed for coordination number determination using the AutoCN program. Dirichlet and ADS programs were employed for Voronoi–Dirichlet polyhedra construction and topological analysis, respectively. The standard structure simplification procedure was employed to obtain the underlying nets of the compounds.

**First-Principles Calculations.** First-principles calculations were performed using the density functional theory (DFT) Vienna Ab-initio Package (VASP) plane-wave code, using the generalized gradient approximation of Perdew, Burke, and Ernzerhof (PBE) and projector augmented wave (PAW) method. For the Na, Cs, P, and S the valence electron configuration considered for construction of PAW potentials are 2p⁶3s², 5s⁵p⁶s⁵, 3s³p⁴, and 3s³p³, respectively. For the rare-earth elements we used the La₆s, Ce₆s, Pr₆s, Nd₆s, and Sm₃ pseudopotentials from the VASP distribution. We chose these potentials because with the other respective pseudopotentials we could not converge the energy even after 200 steps in the SCF cycle. We performed spin-polarized calculations, with 410 eV cutoff energy for the plane wave basis set, and 10⁻⁶ eV energy convergence criteria were used for the calculations. The ground state geometries at 0 K were optimized by relaxing the cell volume, atomic positions, and cell symmetry until the maximum force on each atom is less than 0.001 eV/Å. We used k-point mesh of 3 × 5 × 3 and 3 × 3 × 4 for the ALnPₓS₇ and ALnPₓS₅ structures (A = Na, Cs; Ln = La, Ce, Pr, Nd, Sm), respectively.

**RESULTS AND DISCUSSION**

**Synthesis.** With one exception, all compounds reported herein were obtained as phase pure samples when synthesized under exactly the same flux growth conditions using a CsI–NaI eutectic flux, offering a convenient experimental probe of thermodynamic vs kinetic stability of the crystalline materials in these systems. Arguing from the standpoint of knowing what products formed, we can infer that under the iodide flux synthesis conditions two types of thiophosphate groups are present in the melt, the P(V)₂S₄⁻ and P(IV)₂S₄⁻, the latter resulting from the reduction of phosphorus from +5 to +4. The larger cations La³⁺ and Ce³⁺ favor the formation of NaLa₃P₇ and NaCe₃P₇ compounds belonging to the P2₁/c structure type of the NaLn₂P₇ series. The presence of shiny iodine crystals at the top of the reaction vessels leads to the presumption that the reducing agent in these reactions is the iodide flux, although molecular iodine is typically present in commercial alkali iodide reagents as an impurity. In order to clarify whether or not iodine is essential for the reduction of phosphorus(V) to phosphorus(IV), a reaction utilizing a CsCl/NaCl eutectic flux (melting point 486 °C) was carried out at 550 °C. Unlike the reaction utilizing the CsI/NaI flux, which resulted in the formation of NaN₆P₃S₁₀, the use of the CsCl/NaCl flux did not result in NaN₆P₃S₁₀ but rather in a mixture of Cs₃P₆S₁₀, Cs₃La₃(P₅S₁₀)(PS₂)₂, and a small fraction of Cs₃La₃P₇S₁₀ as identified by a combination of powder and single crystal XRD. The presence of a reduced phosphorus species among the products, i.e., P(S₄)₂⁻ in Cs₃La₃(P₅S₁₀)(PS₂)₂ (which is isostructural with Cs₃La₃P₇S₁₀) and a P(IV)₂S₄⁻ (P(IV)₂S₄⁻ is a preference for missing symmetry with the Addsym program implemented into PLATON software and no higher symmetry was found. The crystallographic data and results of the diffraction experiments are summarized in Tables 1 and 2). The presence of a reduced phosphorus species among the products, i.e., P(S₄)₂⁻ in Cs₃La₃(P₅S₁₀)(PS₂)₂ (which is isostructural with Cs₃La₃P₇S₁₀) and a P(IV)₂S₄⁻ (P(IV)₂S₄⁻ is a preference for missing symmetry with the Addsym program implemented into PLATON software and no higher symmetry was found. The crystallographic data and results of the diffraction experiments are summarized in Tables 1 and 2).
thermodynamically stable phase, we carried out the same reactions with shorter and longer dwelling times of between 1 and 100 h. The decrease of the dwelling time from 20 to 1 h resulted in almost phase pure CsPrP$_5$S$_8$, whereas the longer dwelling time of 100 h favored the formation of pure NaPrP$_5$S$_8$ (Figure 1), suggesting that the former is a kinetic product and the latter is a thermodynamically favored product. In order to probe the formation of the reduced phosphorus NaNdP$_5$S$_8$ phase in the Nd-containing system, we performed a similar reaction with 100 h dwelling time in the Nd system. The PXRD pattern of the products reveals the presence of both the reduced NaNdP$_5$S$_8$ and the CsNdP$_5$S$_8$ thiophosphate phase (Figure S4). It appears that the limiting kinetic step in this reaction is the rate of reaction between the rare earth metal and either the P(V)$_2$S$_6^{-4}$ or P(IV)$_2$S$_6^{-4}$ anion. The fact that the larger rare earth metals favor the formation of the more thermodynamically stable NaLnP$_5$S$_8$ phase over the kinetic CsLnP$_5$S$_8$ phase favored by the smaller lanthanides suggests that the P(V)$_2$S$_6^{-4}$ species reacts faster with the smaller rare earth metals.

The CsI/NaI eutectic flux used in this study has a roughly 1:1 molar ratio of the alkali cations. Aside from the observed structural types, NaLnP$_5$S$_8$ and CsLnP$_5$S$_8$, this could lead to the formation of two other analogs, CsLnP$_5$S$_6$ and NaLnP$_5$S$_6$. Schoop et al. have established that crystals representing the former structure type, CsLaP$_5$S$_6$, can be formed under solid state conditions. Both NaLaP$_5$S$_6$ reported herein, and CsLaP$_5$S$_6$ reported by Schoop, share the same structure type and only exhibit a small difference in the unit cell volumes due to the difference in the alkali cation size. Although both Na$^+$ and Cs$^+$ cations were present in the CsI/NaI eutectic flux reaction, the formation of NaLaP$_5$S$_6$ seemed to be preferred over the formation of CsLaP$_5$S$_6$ under these conditions. One can surmise that Na atoms provide a better fit for the interlayer space between the [LaP$_5$S$_6$]$^-$ layers (see structure description part), resulting in a relatively higher stability of the compounds. Similar speculations would apply to the thiophosphate analogs, NaLnP$_5$S$_6$ and CsLnP$_5$S$_6$, although there are no examples of the sodium compounds deposited in ICSD to enable us to make an actual comparison.

Structure Description. There are two structure types observed in this study, NaLnP$_5$S$_6$ and CsLnP$_5$S$_6$. Early lanthanides, La and Ce, form a NaLnP$_5$S$_6$ composition and crystallize in the monoclinic P2$_1$/c space group. The structure consists of [LnP$_5$S$_6$]$^-$ sheets in the bc plane connected into a framework by the sodium cations located in the interlayer space (Figure 2). The lanthanide cations Ln$^{3+}$ form a distorted capped square antiprism with the Ln–S bond lengths falling into the 2.9648(5)–3.2086(5) and 2.9381(5)–3.2833(6) Å ranges for La and Ce, agreeing well with Ln-S bond lengths previously reported in the literature. Na$^+$–S bond lengths in both structures range from 2.9613(12) to 3.2765(11) Å. Each lanthanide atom is bound to four staggered P$_2$S$_6^{-4}$ units. The matrix–P and P–S bond distances fall within the expected ranges of 2.2024(7)–2.2056(7) and 1.9927(7)–2.0380(7) Å, respectively.

The remainder of the series crystallizes in the CsLnP$_5$S$_8$ structure type, where Ln = Pr–Sm, Gd–Er, Yb. In this structure type, there are corrugated [Ln(P$_5$S$_6$)$_2$]$^-$ layers connected via electrostatic interactions with the interlayer Cs$^+$ cations (Figure 3). In accordance with the known tendency of the late lanthanides to adopt a low coordination number environment, the Ln atoms are eightfold coordinated with a coordination polyhedron in the shape of a distorted square antiprism. The Ln–S distances gradually decrease across the series, ranging from 2.8878(4)–3.0731(4) Å in the structure of CsPrP$_5$S$_6$ to 2.7196(6)–3.1856(7) Å in CsYbP$_5$S$_6$, whereas the P–S–P bond angle barely increases from 110.12(2)$^o$ in CsPrP$_5$S$_6$ to 110.66(3)$^o$ in CsYbP$_5$S$_6$. The decreasing lanthanide cation size is accompanied by a gradual decrease of the unit cell volumes (Tables 1 and 2) from 1154.99(4) to 1108.31(4) Å$^3$. The P–S distances are consistent in all structures and lie within the narrow range of 2.0010(6)–2.0294(7) and 2.1192(13)–2.1269(7) Å for the bonds with terminal and bridging S atoms, respectively. Similar to the NaLnP$_5$S$_6$ series, each lanthanide atom in the structure of the CsLnP$_5$S$_8$ series is connected to four thiophosphate groups, whereas each thiophosphate group is bound by four lanthanide atoms.

![Figure 1. PXRD patterns of the products of a reaction between Pr$_5$S$_6$, Na$_5$S$_6$, and P$_5$S$_6$ (the molar ratio is 1:6:8) in CsI–NaI eutectic flux with the same temperature profile except the dwelling time, which is 1, 20, and 100 h. Long dwelling time favors the formation of the kinetically hindered NaPrP$_5$S$_8$ product, whereas short dwelling time results almost exclusively in the kinetic CsPrP$_5$S$_8$ product.](image1)

![Figure 2. (a) Lanthanum coordination polyhedron and P$_2$S$_6^{-4}$ group in the structure of NaLaP$_5$S$_6$ (b and c) A view on the structure along and perpendicular to the [LaP$_5$S$_6$]$^-$ layers, and (d) their topology. Interlayer sodium atoms are shown in green.](image2)
Both NaLnP$_2$S$_6$ and CsLnP$_2$S$_7$ have similar local topologies; however, their net topologies differ significantly. The underlying net of CsLnP$_2$S$_7$ is a uninodal net with sql (square lattice) topology, whereas NaLnP$_2$S$_6$ structure adopts a topology that consists of two honeycomb nets located one above the other and connected pairwise by vertices (Figure 2d). The Voronoi polyhedra volumes of the lanthanide atoms and their R$_{56,66}$ (the radius of a sphere with the volume of the atom’s Voronoi polyhedra$^{56,66}$) correlate well with the radii of the lanthanide cations (Figure 4).

**DFT Calculations.** To assess the thermodynamic stability of the compounds in both series, we calculated their total energies (Figure 5a,b). A direct comparison between the NaLnP$_2$S$_6$ and CsLnP$_2$S$_7$ (Ln = La, Ce, Pr, Nd, and Sm) series is hindered by their different compositions; however, a general trend can be deduced by taking the La compound in both series as a reference point, since it has the lowest energies in both series. The evident lower energy of the La compounds comes from the different electronic configuration of La and the other rare-earth elements, with La being the only element with no $f$-electrons. As can be seen from Figure 5c, both Ce compounds have virtually the same energy difference with their respective La reference point, which suggests that whichever structure type is more stable in the case of La, is also more stable in the case of Ce. This is supported by the experimental data, i.e., in both La and Ce cases the thiohypophosphate product NaLnP$_2$S$_6$ forms. Upon further increase of the lanthanide size, the energy increment begins to differ for the NaLnP$_2$S$_6$ and CsLnP$_2$S$_7$ cases; i.e., for the former one, the total energy grows faster than for the latter one, meaning that the CsLnP$_2$S$_7$ gradually becomes more stable than the NaLnP$_2$S$_6$ structure type. Given the lanthanide coordination numbers of 9 and 8 in NaLnP$_2$S$_6$ and CsLnP$_2$S$_7$, this trend is in a good agreement with the known tendency of the early lanthanides to adopt coordination polyhedra with higher coordination numbers. As the size of the lanthanide atom decreases across the series, the NaLnP$_2$S$_6$ structure type that contains a Ln site with higher coordination number turns relatively less energetically favorable as compared to the

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**Figure 3.** (a) Praseodymium coordination polyhedron and P$_2$S$_7^{4-}$ group in the structure of CsPrP$_2$S$_7$. (b and c) A view on the structure along and perpendicular to the [P$_2$S$_7^{4-}$]$^{−}$ layers, and (d) their topology. Interlayer cesium atoms are shown in green.

**Figure 4.** Correlation between cation radii of the lanthanides and the Voronoi polyhedra volumes of the lanthanide cation in the structures of CsLnP$_2$S$_7$.$^{56,66}$

**Figure 5.** (a,b) Total energies of the compounds in the NaLnP$_2$S$_6$ and CsLnP$_2$S$_7$ (Ln = La, Ce, Pr, Nd, and Sm) series, respectively. (c) Calculated total energy change along the NaLnP$_2$S$_6$ and CsLnP$_2$S$_7$ series. The total energies of NaLaP$_2$S$_6$ and CsLaP$_2$S$_7$ were taken as a reference point, and the curves, blue for NaLnP$_2$S$_6$ and red for CsLnP$_2$S$_7$ series, show an increase in energy from Ln = Ce to Sm.
CsLnP$_2$S$_6$ structure type, which has a lower coordination number lanthanide site and thus is more favorable for the later (smaller) lanthanides. Supported by the experimental data, one can speculate that the energy becomes roughly identical for NaPrP$_2$S$_6$ and CsPrP$_2$S$_7$ as both compounds can be obtained from the same reaction at different dwelling times, and their transformation to each other is subject to processes obscured by kinetic factors. Further increase in the energy when replacing Pr with Nd puts the energy of NaNdP$_2$S$_6$ compound above the energy of CsNdP$_2$S$_7$, as it can be deduced by the almost exclusive formation of the latter one under the given synthetic conditions.

**Magnetism.** Magnetic susceptibility measurements were performed on the samples with Ln = Ce, Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er, Yb. The magnetic susceptibility vs temperature and inverse magnetic susceptibility vs temperature plots are shown in Figure 6 and Figures S25–S31. All the compounds except CsSmP$_2$S$_7$ follow the Curie–Weiss law and the inverse susceptibility plots were fit to derive the effective magnetic moments and Weiss constants of the materials (Table 3). CsSmP$_2$S$_7$ exhibits Van Vleck magnetism due to a mixture of ground and excited states and, therefore, does not follow the Curie–Weiss law. The inverse susceptibility plot of NaPrP$_2$S$_6$ exhibits curvature at low temperature region, possibly due to crystal field splitting effects of $^3$H$_4$ ground state. The effective magnetic moments of the early lanthanides were derived from the Curie–Weiss law and are slightly larger than the calculated moments for free cations reported in the literature. Moments of 2.84, 3.76, and 4.01 $\mu_B$ vs 2.54, 3.58, and 2.68 $\mu_B$ were obtained for Ce, Pr, and Nd, respectively. The effective magnetic moments for the remainder of the series are in good agreement with the calculated values for the free ions (Table 3).

![Figure 6](image)

Figure 6. Magnetic susceptibility temperature dependence of NaCeP$_2$S$_6$ (left), CsPrP$_2$S$_7$ (middle), and CsSmP$_2$S$_7$ (right).

**Table 3. Effective Magnetic Moments and Weiss Constants for Compounds 2, 4–12**

<table>
<thead>
<tr>
<th></th>
<th>Ce</th>
<th>Pr</th>
<th>Nd</th>
<th>Gd</th>
<th>Tb</th>
<th>Dy</th>
<th>Ho</th>
<th>Er</th>
<th>Yb</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\mu_{eff}$, $\mu_B$</td>
<td>2.84</td>
<td>3.76</td>
<td>4.01</td>
<td>7.86</td>
<td>9.73</td>
<td>10.54</td>
<td>10.59</td>
<td>9.73</td>
<td>4.52</td>
</tr>
<tr>
<td>$\theta$, K</td>
<td>−42.5</td>
<td>−15.3</td>
<td>−44.1</td>
<td>0.0</td>
<td>18.1</td>
<td>7.1</td>
<td>−1.6</td>
<td>−10.9</td>
<td>−33.3</td>
</tr>
<tr>
<td>calculated $\mu_{eff}$, $\mu_B$</td>
<td>2.54</td>
<td>3.58</td>
<td>3.62</td>
<td>7.94</td>
<td>9.72</td>
<td>10.65</td>
<td>10.60</td>
<td>9.58</td>
<td>4.54</td>
</tr>
</tbody>
</table>

CsLnP$_2$S$_6$ structure type, which has a lower coordination number lanthanide site and thus is more favorable for the later (smaller) lanthanides. Supported by the experimental data, one can speculate that the energy becomes roughly identical for NaPrP$_2$S$_6$ and CsPrP$_2$S$_7$ as both compounds can be obtained from the same reaction at different dwelling times, and their transformation to each other is subject to processes obscured by kinetic factors. Further increase in the energy when replacing Pr with Nd puts the energy of NaNdP$_2$S$_6$ compound above the energy of CsNdP$_2$S$_7$, as it can be deduced by the almost exclusive formation of the latter one under the given synthetic conditions.

**Magnetism.** Magnetic susceptibility measurements were performed on the samples with Ln = Ce, Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er, Yb. The magnetic susceptibility vs temperature and inverse magnetic susceptibility vs temperature plots are shown in Figure 6 and Figures S25–S31. All the compounds except CsSmP$_2$S$_7$ follow the Curie–Weiss law and the inverse susceptibility plots were fit to derive the effective magnetic moments and Weiss constants of the materials (Table 3). CsSmP$_2$S$_7$ exhibits Van Vleck magnetism due to a mixture of ground and excited states and, therefore, does not follow the Curie–Weiss law. The inverse susceptibility plot of NaPrP$_2$S$_6$ exhibits curvature at low temperature region, possibly due to crystal field splitting effects of $^3$H$_4$ ground state. The effective magnetic moments of the early lanthanides were derived from the Curie–Weiss law and are slightly larger than the calculated moments for free cations reported in the literature. Moments of 2.84, 3.76, and 4.01 $\mu_B$ vs 2.54, 3.58, and 2.68 $\mu_B$ were obtained for Ce, Pr, and Nd, respectively. The effective magnetic moments for the remainder of the series are in good agreement with the calculated values for the free ions (Table 3). Only one compound, CsGdP$_2$S$_7$, exhibits perfect paramagnetic behavior with a Weiss constant of 0 K. The negative Weiss constants could indicate antiferromagnetic correlations in the compounds with Ln = Ce, Pr, Nd, Ho, Er, Yb, and ferromagnetic correlations when Ln = Tb and Dy, although there are no magnetic transitions observed down to 2 K. Supported by the perfect paramagnetic behavior of the Gd analog, the nonzero Weiss constants of the other compounds in the series could also be explained by crystal electric field effects, which are typical for the lanthanides. The lack of magnetic interactions and magnetic ordering could be expected as the smallest Ln-Ln distance in the structures of the reported compounds is observed for CsHoP$_2$S$_6$, and equals 4.86 Å, which is significantly larger than a distance at which magnetic interactions for highly localized 4f orbitals would be anticipated.

**UV–vis Spectroscopy.** Characteristic f–f transitions were resolved in the absorption spectra of CsLnP$_2$S$_6$ (Ln = Pr–Sm, Tb–Er) and are shown in Figures S13–S19, indicating the localization of the 4f orbitals. As anticipated, no f–f transitions were observed in the spectra of CsYP$_2$S$_7$ and NaLaP$_2$S$_6$ due to the absence of f electrons. Similarly, Ce$^{3+}$ (4f$^1$) and Yb$^{3+}$ (4f$^{13}$) have no f–f transitions, but rather f–d transitions with transition energies in the infrared range. In the case of CsGdP$_2$S$_7$, absorption from the ground state to the lowest energy excited state for the Gd$^{3+}$ ion is expected to occur at approximately 311 nm; thus, no f–f transitions were observed. The absorption spectra of CsLnP$_2$S$_6$ (Ln = Y, Gd, Yb) and NaLaP$_2$S$_6$ (Ln = La, Ce) can be found in the Supporting Information in Figures S20–S24. The diffuse reflectance spectra were converted to optical energy plots to emphasize the presence of sharp absorption edges characteristic of semiconductors. The optical band gaps were estimated to be 3.4 and 2.6 eV for NaLnP$_2$S$_6$ (Ln = La, Ce), respectively, and 3.0 (Y), 3.2 (Pr), 3.2 (Nd), 2.7 (Sm), 3.1 (Gd), 3.1 (Tb), 3.1 (Dy), 3.3 (Ho), 3.1 (Er), and 1.9 (Yb) eV. The calculated band gaps are consistent with the observed colors for each phase.

**CONCLUSION**

A series of lanthanide hexathiohypophosphates and thiopyrophosphates was obtained by high temperature flux crystal growth using an iodide flux. The reactions were performed using the same synthetic conditions and yielded, depending on the size of the lanthanide cation, two structure types or their mixtures, NaLnP$_2$S$_6$ (Ln = La, Ce, and Pr) and CsLnP$_2$S$_6$ (Ln = Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er, and Yb). Obtaining P(IV) from P(VI)$_2$ phase with a reduced P(IV) from P(VI)$_2$ starting material serves as a good example that flux reactions under reducing conditions, i.e., in the presence of $^−$ and $^{32}$O anions, can be accompanied by a reduction step, if the final products are thermodynamically favored. There is a kinetic energy barrier in the formation of NaPrP$_2$S$_6$, which can be overcome by extending the dwelling time of the reaction. The use of iodide flux is therefore a
Convenient route for the synthesis of both kinetically and thermodynamically stable thiophosphates by varying the dwelling time at relatively low temperatures.

With the exception of CsMnP$_2$S$_5$, which shows a characteristic Van Vleck paramagnetic behavior, the magnetic susceptibility all of the obtained materials follows the Curie–Weiss law and the Weiss constants indicate either weak antiferromagnetic or ferromagnetic correlations, although there is no magnetic transitions observed down to 2 K. UV–vis spectra of the obtained materials are in a good agreement with the reference literature data, showing little influence of the coordination environment on the electronic structure of the localized 4f orbitals.

**Associated Content**

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.9b00806.

PXRD patterns, UV–vis spectra, EDS results, and magnetic susceptibility versus temperature plots (PDF)

**Accession Codes**

CCDC 1891155–1891166 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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(1), 195

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