

[P₆Se₁₂]⁴⁻: A Phosphorus-Rich Selenophosphate with Low-Valent P Centers

In Chung, Angela L. Karst, David P. Weliky, and Mercuri G. Kanatzidis*

Department of Chemistry, Michigan State University, East Lansing, Michigan 48824

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The new selenophosphate Rb₄P₆Se₁₂ features the *trans*-decalin-like, [P₆Se₁₂]⁴⁻ anion, a phosphorus-rich species that possesses three parallel P–P bonds and formally P²⁺ and P⁴⁺ centers. The synthesis of Rb₄P₆Se₁₂ was accomplished with the reductive addition of P to RbPSe₆ and represents an interesting example of how alkali chalcophosphates can serve as starting materials to produce new compounds under mild reaction conditions.

The diversity found within the class of metal chalcophosphates is extensive.¹ Typically, these are ternary (M/P/Q) and quaternary (A/M/P/Q) compounds with [P_xQ_y]^{z-} anions in their structure, where M is a metal, A is an alkali metal, and Q is sulfur or selenium. The selenophosphate anions that are structurally characterized include [PSe₄]³⁻,² [PSe₄]³⁻·2Se₆,³ [P₂Se₆]⁴⁻,⁴ [P₂Se₉]⁴⁻,⁵ [P₂Se₁₀]⁴⁻,⁶ [P₈Se₁₈]⁶⁻,⁷ [P₂Se₈]²⁻,⁸ and the one-dimensional polymer ¹/_∞[PSe₆]⁻.⁹ All of these are P⁵⁺ species except for [P₂Se₆]⁴⁻ and [P₈Se₁₈]⁶⁻, which are formally P⁴⁺ and P⁴⁺/P³⁺ compounds with P–P bonds, respectively. Each anion is capable of coordinating to a metal (M) and giving rise to extended structures.^{1,10} Core questions in this chemistry include the limits of structural diversity and the stabilization of species with P in even lower oxidation states. Consequent phosphorus-rich phases have been rare in this chemistry. With this in mind, we conducted experi-

ments aimed at stabilizing alkali salts of chalcophosphate anions by employing new synthetic conditions. In the present case, we attempted reductive reactions using P⁵⁺[P_xQ_y]^{z-} species as starting materials with an excess of elemental P. This chemistry was carried out at ~400 °C with RbPSe₆ and red P and resulted in the new compound Rb₄P₆Se₁₂.

Here we describe the new polar chalcophosphate anion [P₆Se₁₂]⁴⁻,¹¹ featuring P in two different oxidation states of 2+ and 4+. This is manifested in three parallel P–P bonds in the molecule. Direct combination reactions of Rb₂Se, P, and Se with the correct stoichiometric ratio could not produce this compound. The result suggests a unique suitability of alkali chalcophosphates as starting materials to explore new chemistry. This is partly due to their low melting points (300–400 °C) and high reactivity.

The new structure-type of Rb₄P₆Se₁₂¹² adopts the noncentrosymmetric space group *Pca*2₁. The compound features discrete [P₆Se₁₂]⁴⁻ molecules (Figure 1a). The centrosymmetric molecule generates itself through a 2₁-screw axis along the *c* axis with no mirror plane perpendicular to the *c* axis and, consequently, crystallizes in a noncentrosymmetric fashion (Figure 1b). The most unusual feature of the structure is its bicyclic nature and the presence of three P–P bonds with two types of formal charges of P²⁺ and P⁴⁺. The divalent formal charge is found on P2 and P5. The structure of the [P₆Se₁₂]⁴⁻ molecule is reminiscent of the bicycloalkane *trans*-

* To whom correspondence should be addressed. E-mail: kanatzid@cem.msu.edu.

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- (11) Pure Rb₄P₆Se₁₂ was achieved by a mixture of RbPSe₆:P = 1:4 under vacuum in a silica tube at 400 °C for 3 days, followed by washing with degassed *N,N*-dimethylformamide (DMF) under a N₂ atmosphere. Energy-dispersive spectroscopy microprobe analysis showed an average composition of “Rb_{3.9}P₆Se_{11.7}” for five orange irregular-shaped single crystals. The single crystals are stable in acetonitrile, DMF, and deionized water, and they are air-stable for over 1 week.
- (12) Crystal data for Rb₄P₆Se₁₂ at 293(2) K: Siemens SMART Platform CCD diffractometer, Mo K α radiation (λ = 0.710 73 Å), orthorhombic, *Pca*2₁, *a* = 16.409(3) Å, *b* = 10.640(2) Å, *c* = 15.105(3) Å, *V* = 2637.1(9) Å³, *Z* = 4, *D_c* = 3.716 g/cm³, μ = 24.296 mm⁻¹, 2θ = 1.91–28.29°, 22 687 total reflections, 6163 unique reflections with *R*(int) = 0.1274, refinement on *F*², GOF = 0.854, 199 parameters, *R*1 = 4.63%, *wR*2 = 7.69% for *I* > 2 σ (*I*), absolute structure parameter = 0.07(3). An empirical absorption correction was done using SADABS, and all atoms were refined anisotropically. Structure solution and refinement were performed using the SHELXTL package of crystallographic programs. The PLATON program (Spek, A. L. *J. Appl. Crystallogr.* **2003**, *36*, 7) could not suggest additional symmetry, and the structure could not be solved in a centrosymmetric space group such as *Pbcm*.

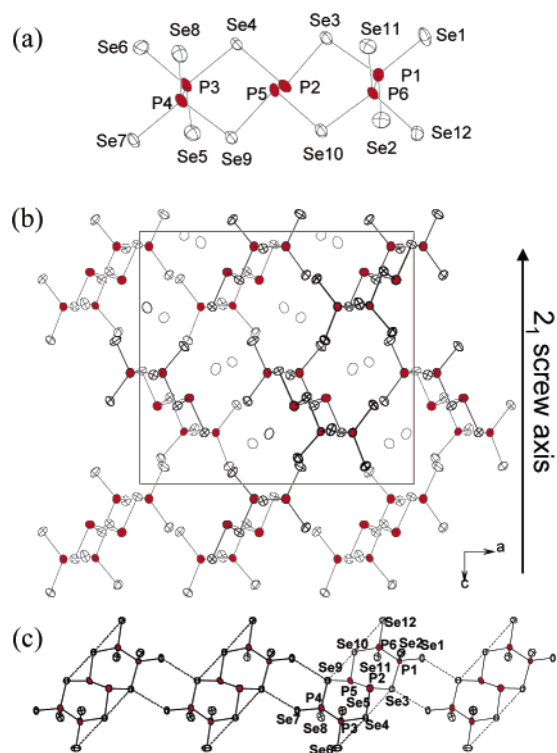


Figure 1. (a) $[P_6Se_{12}]^{4-}$ anion. (b) Structure of $Rb_4P_6Se_{12}$. (c) Pseudo-one-dimensional chain of $[P_6Se_{12}]^{4-}$ via $Se \cdots Se$ nonbonding contacts. Selected bond distances (Å): P1–Se1, 2.128(5); P1–Se2, 2.130(6); P1–Se3, 2.275(6); P2–Se3, 2.288(5); P2–Se4, 2.294(6); P3–Se4, 2.288(5); P3–Se5, 2.116(6); P3–Se6, 2.136(6); P4–Se7, 2.133(5); P4–Se8, 2.128(6); P4–Se9, 2.285(7); P5–Se9, 2.279(5); P5–Se10, 2.300(6); P6–Se10, 2.282(5); P6–Se11, 2.148(6); P6–Se12, 2.136(6); P1–P6, 2.241(7); P2–P5, 2.189(6); P3–P4, 2.257(7). Selected bond angles (deg): Se1–P1–Se2, 118.4(2); Se1–P1–Se3, 104.5(2); Se2–P1–Se3, 111.7(2); Se3–P2–Se4, 92.3(2); Se4–P3–Se5, 113.8(2); Se4–P3–Se6, 101.4(2); Se5–P3–Se6, 118.0(2); Se7–P4–Se8, 120.1(3); Se7–P4–Se9, 103.5(2); Se8–P4–Se9, 111.7(2); Se9–P5–Se10, 90.9(2); Se10–P6–Se11, 112.7(2); Se10–P6–Se12, 101.4(2); Se11–P6–Se12, 118.5(2); P1–P6–Se10, 104.7(2); P1–P6–Se11, 111.1(3); P1–P6–Se12, 107.2(3); P2–P5–Se9, 96.0(2); P2–P5–Se10, 96.7(2); P3–P4–Se7, 105.8(2); P3–P4–Se8, 111.6(3); P3–P4–Se9, 102.5(3); P4–P3–Se4, 103.0(2); P4–P3–Se5, 113.0(2); P4–P3–Se6, 105.9(3); P5–P2–Se3, 94.8(2); P5–P2–Se4, 96.7(2); P6–P1–Se1, 104.7(2); P6–P1–Se2, 112.8(3); P6–P1–Se3, 103.2(2). Dashed lines indicate weak $Se \cdots Se$ nonbonding interactions (Å): Se1 \cdots Se9, 3.384(3); Se3 \cdots Se4, 3.273(3); Se3 \cdots Se7, 3.340(3); Se4 \cdots Se6, 3.413(3); Se9 \cdots Se10, 3.276(3); Se10 \cdots Se12, 3.416. The thermal ellipsoids are shown with 50% probability.

decalin. The central P_2 unit is condensed with two ethane-like $[P_2Se_6]^{4-}$ fragments to form the decalin-like skeleton.

The $[P_6Se_{12}]^{4-}$ molecule adopts the C_{2h} point group, so that the central $[P_2Se_4]$ subunit has a *trans*- C_{2h} -type configuration around the P^{2+} centers. The same *trans*- C_{2h} -type configuration is found in P_2X_4 ($X = F, Cl, I$).¹³ The Se–P–Se angles around P2 and P5 are nearly 90° [Se3–P2–Se4, $92.3(2)^\circ$; Se9–P5–Se10, $90.9(2)^\circ$]. The dihedral angles of Se3–P2–P5–Se9 and Se4–P2–P5–Se10 are $178.76(20)$ and $-179.74(20)^\circ$, respectively. As a result, the P2–P5 vector defines the intersection of two planes. The outer $[P_2Se_6]$ residues in the molecule represent typical anti-type conformations but are distorted. (See relevant angles in the caption of Figure 1.) The P–Se distances are normal at

2.116(6)–2.300(6) Å. The Se–P–Se angles range from $90.9(2)$ to $120.1(3)^\circ$. The P2–P5 distance is 2.189(6) Å, which is only slightly shorter than the typical P–P distance of ~ 2.2 Å in selenophosphates. Rhombohedral black P shows a P–P distance of 2.13 Å.¹⁴

To the best of our knowledge, this is a unique anion. The only other anion with formally P^{2+} centers is the polymeric $1/\infty[P_5Se_{10}^{5-}]$, which is strongly bound to transition-metal atoms in $A_3MP_5Se_{10}$ ($A = K, Rb; M = Ru, Os$).^{15,16} In these compounds, the P^{2+} centers are coordinated to Ru^{2+} or Os^{2+} metal centers through the P atoms, forming P–M bonds ($M = Ru, Os$).

Interestingly, the atoms Se1 \cdots Se3 \cdots Se4 \cdots Se6 are collinear, which allows maximum overlap of their $p\pi$ orbitals. The Se7 \cdots Se9 \cdots Se10 \cdots Se12 atoms are similarly collinear. The intramolecular Se3 \cdots Se4, Se4 \cdots Se6, Se9 \cdots Se10, and Se10 \cdots Se12 distances range from 3.273(3) to 3.416(3) Å and indicate both nonbonding interactions and severely distorted Se–P–Se angles in the central $[P_2Se_4]$ subunit. Similar intramolecular interactions have been observed in the $[PSe_3]$ pyramidal fragment of the $[P_8Se_{18}]^{6-}$ anion and the $1/\infty[PSe_6^-]$ chain in $CsPSe_6$.⁹

Another notable feature is the unusually short intermolecular Se1 \cdots Se9 and Se3 \cdots Se7 distances of 3.384(3) and 3.340(3) Å, respectively. These distances indicate nonbonding interactions, but they are much shorter than the 3.80 Å sum of the van der Waals radii.¹⁷ They enable the molecules of $[P_6Se_{12}]^{4-}$ to organize to an infinite pseudo-one-dimensional structure (Figure 1c). Low-dimensional compounds such as $NbSe_3$ ¹⁸ and $APSe_6$ ($A = K, Rb, Cs$) display similar $Se \cdots Se$ interactions. These intermolecular interactions may contribute to the compound's stability in air and polar solvents such as water and *N,N*-dimethylformamide.

The synthesis of $Rb_4P_6Se_{12}$ adds further insight in the close relationship between the structure and the flux condition (or A:P:Se ratio) in the alkali selenophosphate ternary system. More basic fluxes (i.e., those with a high A:P ratio) or higher reaction temperatures tend to give shorter structural fragments¹⁹ and P in the 5+ oxidation state (Table 1). All simple anions, e.g., $[PSe_4]^{3-}$ and $[P_2Se_9]^{4-}$, were prepared in strongly basic fluxes (Table 1). As the basicity decreases, more complex species emerge, such as $[P_2Se_6]^{4-}$, $[P_8Se_{18}]^{4-}$, and $[P_2Se_8]^{2-}$. Under even less basic flux conditions, the one-dimensional polyselenide chain $1/\infty[PSe_6^-]$ is stabilized with K, Rb, and Cs. $Rb_4P_6Se_{12}$ is made in intermediate acidic/basic conditions, and it contains P^{2+} centers because of excess P.

Differential thermal analysis (DTA) on $Rb_4P_6Se_{12}$ at a rate of $10^\circ C/min$ showed melting at $\sim 431^\circ C$ and crystallization

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Table 1. Relationship between Observed Selenophosphate Species and the A:P:Se Ratio^a

known compounds	anion	A:P:Se ratio ^b	flux condition	note
A ₃ PSe ₄ (A = Na, K, Cs ¹⁶)	[PSe ₄] ³⁻	3:1:4	basic	discrete molecular
Cs ₄ P ₂ Se ₁₀	[P ₂ Se ₁₀] ⁴⁻	2:1:5		
A ₄ P ₂ Se ₉ (A = K, Rb, Cs)	[P ₂ Se ₉] ⁴⁻	2:1:4.5		
A ₄ P ₂ Se ₆ (A = Na, K ¹⁶)	[P ₂ Se ₆] ⁴⁻	2:1:3		
A ₆ P ₈ Se ₁₈ (A = K, ⁷ Rb, Cs ¹⁶)	[P ₈ Se ₁₈] ⁶⁻	1:1.33:3	intermediate	
Rb ₄ P ₆ Se ₁₂	[P ₆ Se ₁₂] ⁴⁻	1:5:6		double six-membered ring
Cs ₂ P ₂ Se ₈	[P ₂ Se ₈] ²⁻	1:1:4	“acidic”	six-membered ring
K ₂ P ₂ Se ₆	¹ _∞ [P ₂ Se ₆] ²⁻	1:1:3		one-dimensional chain
APSe ₆ (A = K, Rb, Cs)	¹ _∞ [PSe ₆] ⁻	1:1:6		

^a All compounds have been structurally refined by single-crystal X-ray diffraction. ^b These are typical ratios. In fact, there are ranges in these ratios that define a given flux condition and can lead to the compounds shown.

upon cooling at ~384 °C. X-ray diffraction patterns for samples before and after DTA were identical. The results suggest that Rb₄P₆Se₁₂ could be a promising precursor in synthesis for further reaction chemistry. The UV–vis spectrum reveals a sharp absorption edge and a band gap of 2.25 eV, which is in good agreement with its orange color. By comparison, the one-dimensional RbPSe₆ with P⁵⁺ showed a gap of 2.18 eV. The Raman spectrum of Rb₄P₆Se₁₂ shows shifts at 218 (vs), 298 (vw), 348(w), 371 (w), 414 (w), 487 (w), and 516 (vw) cm⁻¹. The peak at 218 cm⁻¹ is unambiguously assigned to the locally A_{1g} symmetric stretching mode of PSe₃.²⁰ The second shift at 298 cm⁻¹ resembles the ν₁₂ (B_g) mode in Pb₂P₂Se₆ having C_{2h} site symmetry.²¹ The other vibrations can be attributed to PSe₃ stretching modes.^{4,22} The far-IR spectrum is rather complex, showing peaks at 214 (vs), 238 (bw), 301 (vw), 319 (vw), 353 (vw), 374 (vw), 392 (vw), 408 (w), 464 (vw), 486 (vw), 514 (w), and 524 (w) cm⁻¹. The peak at 319 cm⁻¹ is assigned to a P–P vibration and was not observed in the Raman spectrum. Other peaks are well matched with those of Pb₂P₂Se₆ and other compounds that contain the [P₂Se₆]⁴⁻ anion.²³

Figure 2 displays the ³¹P NMR spectrum of Rb₄P₆Se₁₂. The narrow line widths afford resolution of most of the P sites. The ratio of the integrated intensity of the B–E cluster of peaks to the intensity of peak A is ~2 and is generally consistent with the assignment of P1, P3, P4, and P6 to the B–E peaks and P2 and P5 to the A peak. P1/P6 and P3/P4 *J* couplings are expected, and analysis of the spectrum yielded the same *J* coupling for doublets B and E and the same *J* coupling for doublets C and D. The isotropic chemical shifts and *J* couplings were confirmed by the analysis of

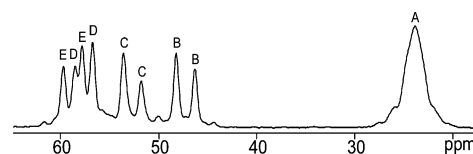


Figure 2. Bloch decay ³¹P NMR spectrum of Rb₄P₆Se₁₂ taken at ambient temperature on a 9.4-T spectrometer. Acquisition parameters included a 5-μs π/2 pulse, a 8000-s relaxation delay, and a 13-kHz magic-angle-spinning frequency. The chemical shift reference was 85% H₃PO₄ (0 ppm). Peaks with the same letter are *J*-coupled. The average chemical shifts of peaks A–E are in the order 23.9, 47.5, 52.6, 57.6, and 58.8 ppm. The *J* couplings of doublets B–E are 309, 292, 295, and 309 Hz.

spectra taken on a 7-T spectrometer. It was not possible to make a more detailed assignment of P1/P6 and P3/P4 to the C/D and B/E doublets, and the P2/P5 shifts were not resolved from one another. The ³¹P NMR chemical shifts are all >0 ppm and are consistent with the positive chemical shifts of other metal selenophosphates with P–P bonding.²⁴

The discovery of the molecular salt Rb₄P₆Se₁₂ with its unique bicycloselenophosphate anion and rare combination of P²⁺ and P⁴⁺ centers suggests a more extensive compositional diversity in alkali chalcophosphates. The unraveling relationship between basicity and the final structure enhances the understanding of flux chemistry and the prospects of the future discovery of new materials in this class of solids.

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Supporting Information Available: X-ray crystallographic file (in CIF format) as well as UV–vis, FTIR, and Raman spectra. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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**[P₆Se₁₂]⁴⁻: A Phosphorus-rich Selenophosphate
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Department of Chemistry, Michigan State University, East Lansing, MI 48824.

Supplementary Information

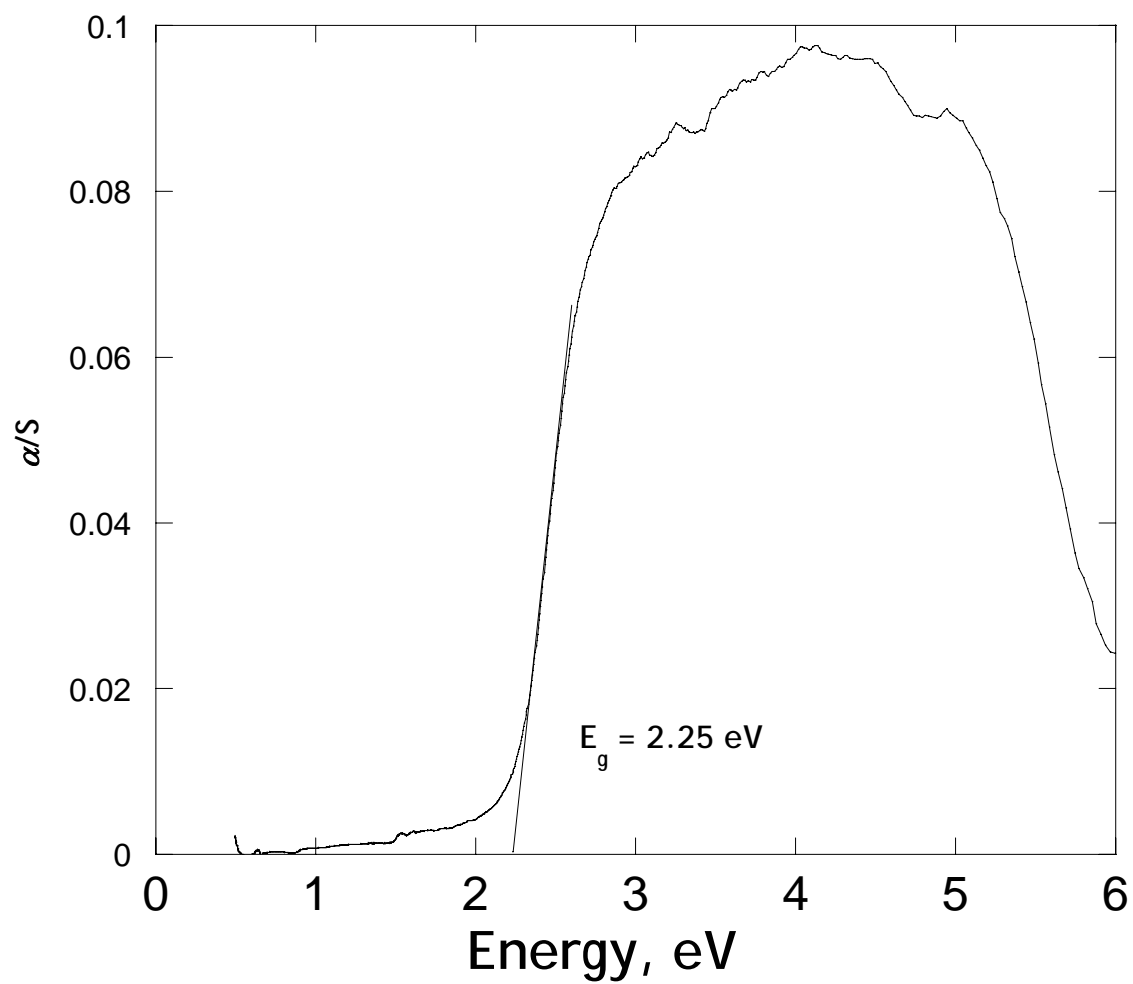


Fig. 1S: Solid state optical absorption spectrum of $\text{Rb}_4\text{P}_6\text{Se}_{12}$.

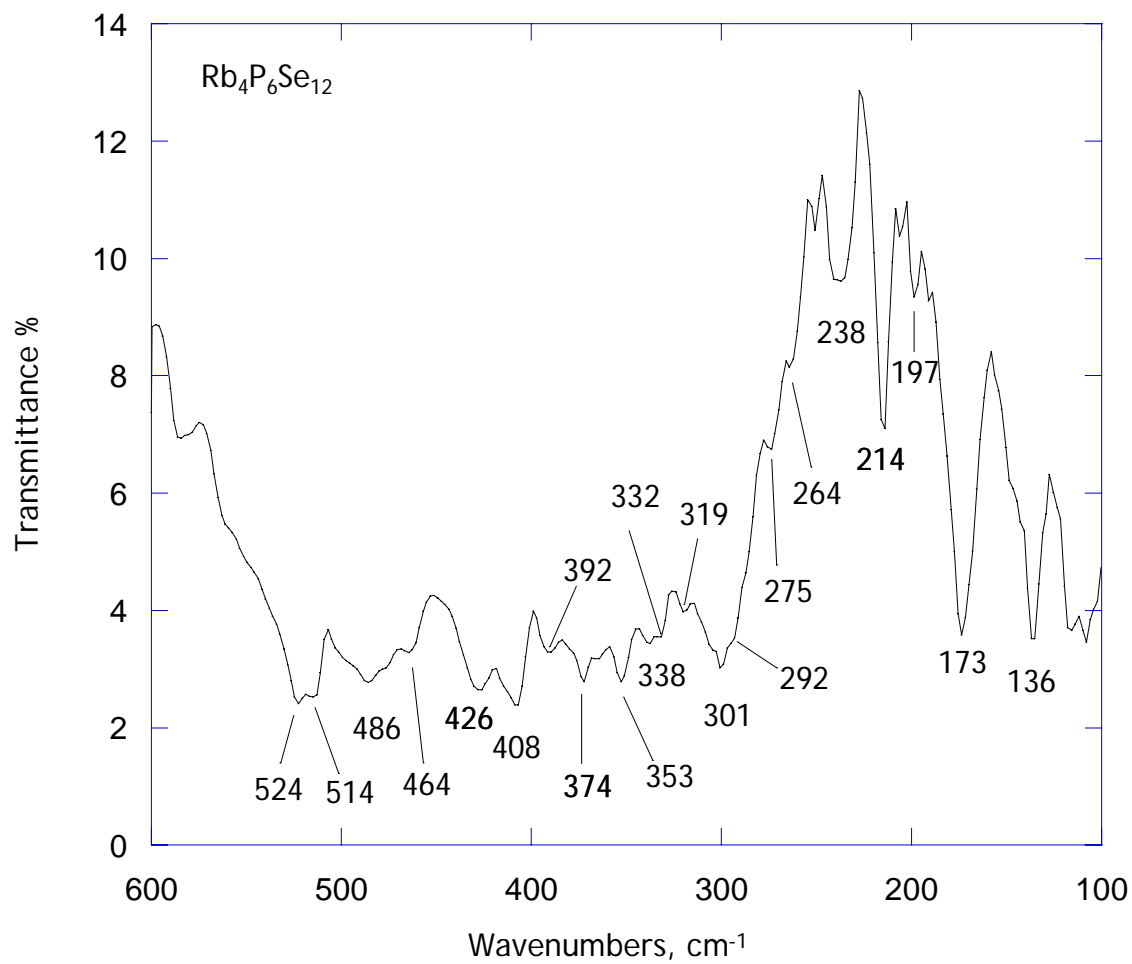


Fig. 2S: Infrared absorption spectrum of $\text{Rb}_4\text{P}_6\text{Se}_{12}$.

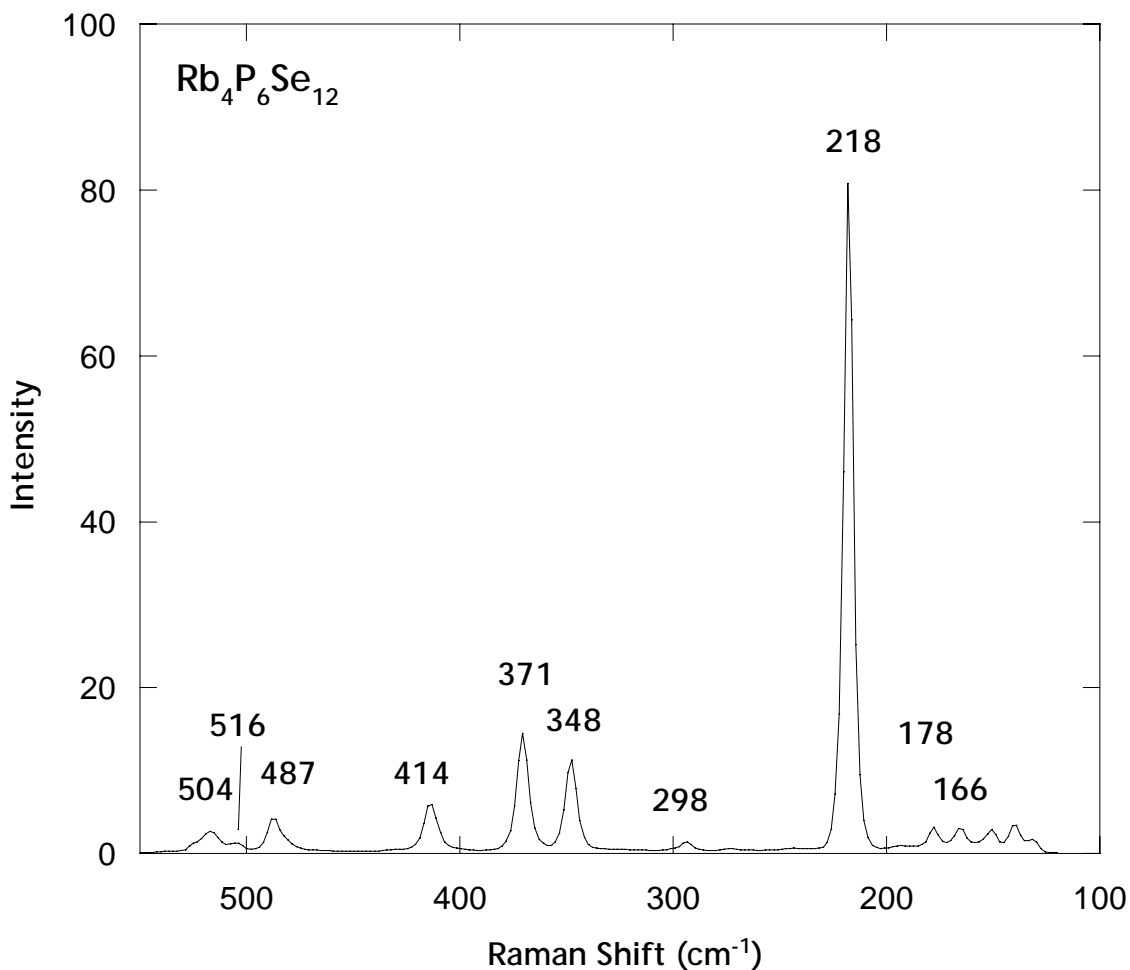


Fig. 3S: Fourier transform Raman spectrum of $\text{Rb}_4\text{P}_6\text{Se}_{12}$.

Solid-state UV-vis/Near IR Spectroscopy. Optical diffuse reflectance measurements were made at room temperature using a Shimadzu UV-3101 PC double beam, double-monochromator spectrophotometer operating in the 200-2500 nm region. The instrument is equipped with an integrating sphere and controlled by a personal computer. BaSO_4 was used as a 100% reflectance standard. The sample was prepared by grinding the crystals intimately to a powder and spreading it on a compacted surface of the powdered standard material, preloaded into a sample holder. The reflectance versus wavelength data generated were used to estimate the band gap of the material by converting reflectance to absorption data.

Infrared Spectroscopy. FT-IR spectrum was recorded as solids in a CsI matrix. The crystals were ground with dry CsI into a fine powder and pressed into translucent pellets. The spectrum was recorded in the far-IR region ($600\text{-}100\text{ cm}^{-1}$, 4 cm^{-1} , resolution) with the use of a Nicolet 740 FT-IR spectroscopy equipped with a TGS/PE detector and silicon beam splitter.

Raman Spectroscopy. Raman spectrum was recorded on a Holoprobe Raman spectrograph equipped with a CCD camera detector using 633 nm radiation from a HeNe laser for excitation and a resolution of 4 cm^{-1} . Laser power at the sample was estimated to be about 5 mW, and the focused laser beam diameter was ca. $10\ \mu\text{m}$. A total of 128 scans was sufficient to obtain good quality spectra.