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$LiEuPSe_4$ and $KEuPSe_4$: Novel Selenophosphates with the Tetrahedral $[PSe_4]^{3-}$ Building Block

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$LiEuPSe_4$, the first quaternary lithium-containing selenophosphate, was synthesized as red polyhedra by reacting Eu with a molten mixture of $Li_2Se/P_2Se_5/Se$ at 750 °C. Similarly, the reaction of Eu with a molten mixture of $K_2Se/P_2Se_5/Se$ at 495 °C produced red polyhedral crystals of $KEuPSe_4$. Both compounds are unstable in moist air. In addition, both compounds were plagued with crystal twinning. Acceptable crystal structure refinements could only be obtained by identifying the type of twinning and taking it into account in the final refinement. $LiEuPSe_4$ crystallizes in the noncentrosymmetric space group *Ama*2 (no. 40) with $a = 10.5592$ (9) Å, $b = 10.415$ (1) Å, $c = 6.4924$ (7) Å, and $Z = 4$. The structure is three-dimensional and composed of $EuSe_8$ distorted square antiprisms and PSe_4 tetrahedral building blocks that create tunnels, running down the *a* axis, in which the Li ions reside. The Li ions are in a highly distorted tetrahedral coordination. $KEuPSe_4$ crystallizes in the space group $P2_1/m$ (no. 11) with $a = 6.8469(6)$ Å, $b = 6.9521(6)$ Å, $c = 9.0436(8)$ Å, $\beta = 107.677(2)°$, and $Z = 2$. The structure has two-dimensional character with layers composed of $EuSe_6$ trigonal prisms and PSe_4 tetrahedral units. Between the $[EuPSe_4]_n^{n-}$ layers the K ions reside in a bicapped trigonal prism of Se atoms. The structure of the $[EuPSe_4]_n^{n-}$ framework is similar to that found in $CsPbPSe_4$. Both compounds are semiconductors with band gaps of 2.00 and 1.88 eV, respectively. Differential thermal analysis and infrared spectroscopic characterization are also reported.

Introduction

The first compound reported from an $A_xP_yQ_z$ (A = alkali metal; Q = S or Se) flux reaction at intermediate temperatures was $ABiP_2S_7$ (A = K, Rb).[1] In the six years since then, others[2−4] and we[5] have undoubtedly demonstrated the use of polychalcophosphate fluxes as an important foundation for the exploratory synthesis of ternary and quaternary thiophosphate and selenophosphate compounds. The polychalcophosphate fluxes are formed by simple *in situ* fusion of $A_2Q/P_2Q_5/Q$. This results in well defined, discrete $[P_yQ_z]^{n-}$ anionic fragments that serve as the basic building blocks required to form new chalcophosphate solids. It is conceptually possible to form any such $[P_yQ_z]^{n-}$ ligand *in situ*, with the only limitation being that it have a modest stability in the flux.

Recently, we investigated the $M/A_2Se/P_2Se_5/Se$ (M = Pb, Eu; A = K, Rb, Cs) systems motivated by a number of reasons explained previously.[6] These investigations have continued further into the K systems and, for the first time, into systems using Na and Li. Finding quaternary compounds containing Na and Li is more difficult because as the size of the alkali metal decreases, the basicity of the flux decreases as well as the probability that the alkali metal will be incorporated into the final product.[7] Thus, Li is the hardest to incorporate and generally requires highly basic conditions. In fact, to the best of our knowledge, $LiEuPSe_4$, reported here, is the first quaternary, lithium-containing selenophosphate. In general there are very few structurally characterized ternary and quaternary lithium-containing selenides, for example, $Li_{0.33}TiSe_2$,[8] $Li_{3.2}Mo_6Se_8$,[9] $LiInSe_2$,[10] ALiSe (A = Na, K, Rb),[11−13] and $Li(Cu, Fe)_{1.073}Se_2$.[14] While there are a few more lithium-containing sulfides, the only structurally characterized quaternary thio-

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phosphate is $Li_xNi_{2-y}P_2S_6$. The last was prepared chemically or electrochemically using $Ni_2P_2S_6$ as the cathode.[15]

In this study, we discovered three new compounds, $LiEuPSe_4$, $Na_{1.5}Pb_{0.75}PSe_4$,[16] and $KEuPSe_4$. These compounds feature the tetrahedral $[PSe_4]^{3-}$ unit, which until recently we referred to as rare and occurring in only a handful of compounds such as Cu_3PSe_4,[17] Tl_3PSe_4,[18] and the molecular $[WSe(PSe_2)(PSe_4)]^{2-}$.[19] Indeed the occurrence of the $[PSe_4]^{3-}$ unit in selenophosphates made from traditional solid-state chemistry techniques is rare. However, more and more we have been able to stabilize this ligand in an $A_xP_ySe_z$ flux.[6,20−23]

Here, we report the synthesis, structure, and optical properties of $LiEuPSe_4$, the first quaternary lithium-containing selenophosphate, and $KEuPSe_4$. We also investigated systems with sodium; however, as of yet we did not find any Na/Eu/P/Se compounds. Besides having the $[PSe_4]^{3-}$ tetrahedral unit in common, both $LiEuPSe_4$ and $KEuPSe_4$ exhibited crystal twinning, and a structure solution could only be properly refined by determining the nature of the twinning and the twin law and taking this into account in the final refinement. While $LiEuPSe_4$ is a three-dimensional compound, $KEuPSe_4$ has two-dimensional character. In moving from Cs to Li, we observe a counterion effect where the smaller the alkali metal the higher the dimensionality of the compound. Furthermore, in a particular system one also observes that the more alkali metal that can be incorporated in the final product, the lower the resulting dimensionality.[24] These relationships will be discussed in greater detail later.

Experimental Section

Reagents. The chemicals in this work were used as obtained as follows unless noted otherwise: (i) europium metal powder 99.9%, <250 μm, Alfa Aesar, Ward Hill, MA, or europium metal chunk 99.9% (the europium metal chunk was cut into fine shavings with a hack saw before being used), Chinese Rare Earth Information Center, Inner Mongolia, China; (ii) lithium metal rods, 99.9%, 12.7 mm diameter, Aldrich Chemical Co., Inc., Milwaukee, WI; (iii) potassium metal, analytical reagent, Aldrich Chemical Co., Milwaukee, WI; (iv) red phosphorus powder, 100 mesh, EM Science, Gibbstown, NJ; (v) selenium powder 99.5+%, 100 mesh, Aldrich Chemical Co., Inc., Milwaukee, WI, or selenium shots 99.999% (the selenium shots were ground to a fine powder before being used), Noranda Advanced Materials, Quebec, Canada; (vi) *N*,*N*-dimethylformamide 99.8%, ACS reagent, Aldrich Chemical Co., Inc., Milwaukee, WI; (vii) diethyl ether, ACS Grade, anhydrous, Columbus Chemical Industries, Inc., Columbus, WI.

Synthesis of Li_2Se and K_2Se. Li_2Se and K_2Se were prepared using a modified literature procedure.[25,26] Powder X-ray diffraction patterns were obtained to confirm the purity of these starting materials.

Synthesis of P_2Se_5. The amorphous phosphorus selenide glass "P_2Se_5" was prepared by heating 4.068 g (0.131 mol) of red phosphorus powder and 25.930 g (0.328 mol) of selenium powder in an evacuated Pyrex ampule for 24 h at 460 °C. The glass was ground up and stored in a nitrogen-filled glovebox.

Preparation of $LiEuPSe_4$. In a nitrogen-filled glovebox, 0.167 g (1.8 mmol) of Li_2Se, 0.046 g (0.3 mmol) of Eu, 0.274 g (0.6 mmol) of P_2Se_5, and 0.190 g (2.4 mmol) of Se was loaded into a Pyrex tube. The tube was sealed under vacuum (approximately 2×10^{-4} mbar) and placed in a programmable furnace. The temperature was raised from 50 to 750 °C over 24 h. This temperature was maintained for 96 h and then decreased at a rate of 3 °C/h to 250 °C. Next, the tube was rapidly cooled to 50 °C in 1 h. The product was isolated by washing away the excess flux, under an atmosphere of nitrogen, with *N*,*N*-dimethylformamide (DMF) and washed with ether. The product consisted of red polyhedral and orange polyhedral crystals (70/30% yield). Semiquantitative energy dispersive analysis (EDS) using a scanning electron microscope (SEM) on several of the red polyhedra indicated the presence of Eu, P, and Se. Lithium cannot be detected by EDS. The orange polyhedra also showed the presence of Eu, P, and Se but in a different ratio. The powder diffraction pattern of only the orange polyhedra indexed to $Eu_2P_2Se_6$,[27] while the powder diffraction pattern of the red polyhedra indicated a new phase.

Preparation of $KEuPSe_4$. (a) Method I: In a K_2Se_x Flux. In a nitrogen-filled glovebox, 0.094 g (0.6 mmol) of K_2Se, 0.091 g (0.6 mmol) of Eu, 0.137 g (0.3 mmol) of P_2Se_5, and 0.237 g (3.0 mmol) of Se were loaded into a Pyrex tube. The tube was flame-sealed under vacuum (approximately 2×10^{-4} mbar) and inserted into a programmable furnace. The temperature was increased from 50 to 495 °C in 24 h. It was held there for 96 h and then decreased at a rate of 1.5 °C/h to 295 °C followed by cooling 10 °C/h to 50 °C. The product was isolated in the same manner as $LiEuPSe_4$ and was red polyhedral crystals. Semiquantitative energy dispersive analysis using a scanning electron microscope on a number of the red polyhededra indicated the presence of all four elements. The powder diffraction pattern indicated a new phase.

(b) Method II: Stoichiometric Reaction. If large crystals are not necessary, the following preparation can be used. In a nitrogen-filled glovebox, 0.047 g (0.3 mmol) of K_2Se, 0.091 g (0.6 mmol) of Eu, 0.137 g (0.3 mmol) of P_2Se_5, and 0.047 g (0.6 mmol) of Se were loaded into a Pyrex tube. The tube was heated in the same manner as in method I, and the product was also isolated in a similar manner. In this case, there should be no residual flux to be dissolved, but DMF did help dislodge the product from the tube. Very small red crystals and red powder were obtained. X-ray powder diffraction gave the same pattern as observed using method I.

Physical Measurements. (a) X-ray Powder Diffraction. Analyses were performed using a calibrated Rigaku-Denki/RW400F2 (Rotaflex) rotating anode powder diffractometer controlled by an IBM computer, operating at 45 kV/100 mA and with a 1°/min scan rate and employing Ni-filtered Cu radiation in a Bragg−Brentano geometry. Observed powder patterns were compared with powder patterns that were calculated with the Cerius2 software package.[28]

(b) Electron Microscopy. Quantitative microprobe analysis of the compounds were performed with a JEOL JSM-35C scanning electron microscope equipped with a Tracor Northern energy dispersive spectroscopy detector. Data were acquired with an accelerating voltage of 20 kV and a 40 s accumulation time.

(c) Differential Thermal Analysis. Differential thermal analysis (DTA) was performed with a computer-controlled Shimadzu DTA-50

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thermal analyzer. Approximately 25 mg of the sample was sealed in a carbon-coated quartz ampule under vacuum. A quartz ampule containing alumina of equal mass was sealed and placed on the reference side of the detector. The sample was heated to 850 °C at 10 °C/min, then isothermed for 5 min, and then cooled at a rate of 10 °C/min to 100 °C followed by rapid cooling to room temperature. Residues of the DTA experiment were examined by powder X-ray diffraction. To evaluate congruent melting, we compared the powder X-ray diffraction patterns before and after the DTA experiments. The stability and reproducibility of the samples were monitored by running multiple heating and cooling cycles.

(d) Single-Crystal UV/Vis. Optical transmission measurements were made at room temperature on single crystals using a Hitachi U-6000 microscopic FT spectrophotometer with an Olympus BH-2 metallurgical microscope over a range 380−900 nm. Because the compound was air-sensitive, the crystals were placed on a glass slide and covered with mineral oil.

(e) Solid-State UV/Vis/Near-IR Spectroscopy. Optical diffuse reflectance measurements were performed at room temperature using a Shimadzu UV-3101PC double-beam, double-monochromator spectrophotometer. 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 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.[29]

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

(g) Single-Crystal X-ray Crystallography. (g.1) $LiEuPSe_4$. A polyhedral-shaped crystal with dimensions 0.20 mm × 0.15 mm × 0.10 mm was sealed under a nitrogen atmosphere in a glass capillary with a wall thickness of 0.01 mm. A Siemens SMART Platform CCD diffractometer at Michigan State University, operating at room temperature and using graphite-monochromatized Mo Kα radiation, was used for data collection. No initial cell is needed in order to collect data using this procedure. The data collection technique is known as hemisphere collection. Here, a region of reciprocal space was surveyed to the extent of 1.3 hemispheres to a resolution of 0.75 Å. A set of 1260 frames were collected with 0.30° steps in ϕ and an exposure time of 30 s/frame, giving a total measurement time of less than 13 h. A ϕ scan technique was used instead of the usual ω scan because there is less chance of a collision between the capillary and the instrument. Attempts to index a unit cell with the SMART[30] indexing routine were met with difficulty. Pseudomerohedral twinning of the nearly metrical tetragonal, orthorhombic unit cell was suspected. This was confirmed by using the alternative indexing program TWINDX,[31] which found two twin components related by the twin law (1, 0, 0/0, −0.015, −0.985/0, −1.015, 0.015). The twin component judged to be of greater mass was used in all subsequent calculations. The cell obtained for the major component was used to integrate the data using SAINT.[30] The final cell constants were determined from a set of ∼1200 strong reflections obtained from data collection. An amount of 1282 reflections were collected in the θ range 3.70−27.27° ($-13 \le h \le 13$, $-12 \le k \le 10$, and $-7 \le l \le 6$). Of these reflections, 629 were unique with $R_{int} = 0.0547$.

An empirical absorption correction was done using SADABS,[32] and all refinements were done with SHELXTL.[33] The systematic absences pointed to three possible space groups: *Cmc*2_1, *Cmcm*, and *Ama*2. Both *Cmc*2_1 and *Ama*2 are noncentrosymmetric, while *Cmcm* is centrosymmetric. The intensity statistics indicated a noncentrosymmetric space group. No solution was obtained in *Cmc*2_1, but *Ama*2 did provide a solution that revealed all atoms within two rounds of least-squares/difference Fourier cycles. One lithium, one europium, one phosphorus, and two selenium atoms were found to occupy special positions, while a third selenium atom was located in a general position. In the initial stages of refinement it was determined that the incorrect enantiomorph was selected. The coordinates were inverted, and the refinement proceeded. A refinement with anisotropic displacement parameters for all atoms led to R1 = 0.0652 and wR2 = 0.1733. The lithium atom did not refine well because the U_{11} and U_{22} were high while the U_{33} was almost zero. It was determined that the lithium atom was librating in a tunnel, and thus, isotropic refinement seemed much more reasonable. The final refinement gave R1 = 0.0503 and wR2 = 0.1245. The maximum and minimum peaks on the final Fourier difference map corresponded to 2.866 and −1.899 $e^-/Å^3$. The final extinction coefficient was 0.009(1). Since the final refinement was adequate, the minor component was considered insignificant, and thus, no corrections for the twinning were made (see Table 1 for a summary of crystallographic data and Table 2 for fractional atomic coordinates and isotropic thermal parameters). A complete table of crystallographic data and anisotropic displacement parameters are deposited as Supporting Information.

Table 1. Crystallographic Data for $LiEuPSe_4$ and $KEuPSe_4$[a]

empirical formula	$LiEuPSe_4$	$KEuPSe_4$
space group	*Ama*2 (no. 40)	$P2_1/m$ (no. 11)
a (Å)	10.5592 (9)	6.8469(6)
b (Å)	10.415 (1)	6.9521(6)
c (Å)	6.4924 (7)	9.0436(8)
β (deg)		107.677(2)°
V ($Å^3$)	714.0(1)	410.15(6)
Z	4	2
fw	505.71	537.87
calcd density (Mg/m^3)	4.705	4.355
abs coeff (mm^{-1})	29.273	25.990
wavelength (Å)	0.710 73	0.710 73
θ range for data collection (deg)	3.70−27.27	2.36−25.03
temp (K)	300	173
R indices ($I > 2\sigma(I)$)	R1 = 0.0503 wR2 = 0.1245	R1 = 0.0516 wR2 = 0.1200
R indices (all data)	R1 = 0.0510 wR2 = 0.1250	R1 = 0.0583 wR2 = 0.1242

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. $wR2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$. $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$. $P = [2F_c^2 + \max(F_o^2,0)]/3$. For $LiEuPSe_4$ $a = 0.0784$ and $b = 0$. For $KEuPSe_4$ $a = 0.0655$ and $b = 0$.

(g.2) $KEuPSe_4$. A platelike crystal having dimensions of 0.26 mm × 0.20 mm × 0.015 mm was frozen in oil on a glass fiber by the cryogenic nitrogen stream. Single-crystal X-ray diffraction data were collected at The University of Minnesota on a Siemens SMART operating at 173 K, with monochromatized Mo Kα radiation. The standard SMART[30] indexing routine failed to provide a unit cell. Nonmerohedral twinning was suspected. DIRAX[34] provided a solution for two twin components in the monoclinic crystal system. A region of reciprocal space was surveyed to the extent of 1.5 hemispheres to a resolution of 0.84 Å. Three sets of frames were collected with 0.30° steps in ω and an exposure time of 10 s/frame, giving a total data collection time of less than 7 h.

Integration of the frame data using SAINT[30] was done in two steps for each twin. The data were integrated fully to achieve a reciprocal matrix based on as many reflections as possible for each. This was then used for final integration without stepwise refinement of the reciprocal matrix. The final cell constants were determined from a set of ∼1500 strong reflections from the data collection. An amount of

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Table 2. Atomic Coordinates and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for $LiEuPSe_4$ and $KEuPSe_4$

atom	Wycoff letter & multiplicity	*x*	*y*	*z*	*U*(eq)[a]
		$LiEuPSe_4$			
Li	4a	0.5000	0.0000	0.392(9)	1(6)
Eu	4a	0.5000	0.0000	0.8863(3)	16(1)
P	4b	0.2500	0.2788(5)	0.866(1)	11(1)
Se(1)	4b	0.2500	0.0980(2)	0.6846(4)	11(1)
Se(2)	4b	0.7500	0.0628(3)	1.1425(4)	17(1)
Se(3)	8c	0.5797(2)	0.2246(2)	0.5617(3)	18(1)
		$KEuPSe_4$			
K	2e	0.7735(8)	0.2500	0.0695(6)	19(1)
Eu	2e	0.7287(2)	0.2500	0.5475(1)	13(1)
P	2e	0.3015(9)	0.2500	0.6963(6)	8(1)
Se(1)	2e	1.0993(3)	0.2500	0.8450(3)	13(1)
Se(2)	2e	1.1298(3)	0.2500	0.4471(3)	16(1)
Se(3)	4f	0.4951(2)	0.0018(2)	0.2558(2)	12(1)

[a] *U*(eq) is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

2101 reflections were collected for one of the twin components, while 2116 reflections were collected for the other. The data were in the θ range 2.36−25.03° ($-8 \le h \le 7$, $-8 \le k \le 8$, and $-10 \le l \le 10$). The unique reflections were 743, with $R_{int} = 0.0581$ for one twin component and $R_{int} = 0.0635$ for the other. The twin law for this specimen was determined to be (1, 0, 0/0, −1, 0/−0.8, 0, −1). The twin law implies that *hkl* reflections with $h = 5n$, where $n = -1, 0, 1$, have exact overlaps. The next worst group of reflections is *h* where $n = \pm1, \pm4, \pm6$. These reflections partially overlap (separated by 0.023 $Å^{-1}$).

SADABS[32] was used to correct for absorption on both reflection lists, and all refinements were performed using the SHELXTL[33] package of crystallographic programs. The space group $P2_1/m$ was determined on the basis of systematic absences and intensity statistics. One potassium atom, one europium atom, one phosphorus atom, and two selenium atoms were found to occupy special positions, while one selenium atom was situated on a general position. At this point the R1 was approximately 0.17. To improve the refinement a SHELXL HKLF 5 reflection file was necessary to correct for the twinning of the specimen.[35] UNTWIN[36] was used to write an HKLF 5 data file, which corrected both exactly and partially overlapped reflections. A separate set of batch scale factors was refined for the partially overlapped reflections. The residuals greatly improved and all atoms were refined with anisotropic displacement parameters to obtain an acceptable final solution, where R1 = 0.0516 and wR2 = 0.1200. The maximum and minimum peaks on the final Fourier difference map corresponded to 3.674 and −3.098 $e^-/Å^3$. The final extinction coefficient was 0.008(3) (see Table 1 for a summary of crystallographic data and Table 2 for fractional atomic coordinates and isotropic thermal parameters). A complete table of crystallographic data and anisotropic displacement parameters are deposited as the Supporting Information.

Results and Discussion

Synthesis and Thermal Analysis. In the chemistry reported here, europium is oxidized by polychalcogenide ions in the $A_x[P_yQ_z]$ flux, forming Eu^{2+} ions. These cations are then coordinated by the highly charged $[P_yQ_z]^{n-}$ ligands to form new selenophosphate compounds. More specifically, $LiEuPSe_4$ forms from a molten mixture of $Eu/Li_2Se/P_2Se_5/Se$ in a 1:6:2:8 molar ratio at 750 °C for 4 days. This compound features the $[PSe_4]^{3-}$ tetrahedral unit, whose occurrence in solid state compounds is relatively uncommon. There are many more compounds containing the $[P_2Se_6]^{4-}$ unit, which suggests that the P^{5+} species is unstable with respect to P^{4+} species under conventional synthetic conditions. However, in the thiophosphate systems, P^{5+} is quite common, and often compounds containing it can be made by direct combination of the elements. This difference is due in part to the fact that S^{2-} does not have as great a reducing powder as does Se^{2-}. The synthesis of $LiEuPSe_4$ is an example of how the flux and our ability to tune its reactivity can enable the synthesis of compounds not usually obtainable by traditional methods. Attempts to synthesize $LiEuPSe_4$ by direct combination of the elements failed, and orange polyhedral crystals of $Eu_2P_2Se_6$[27] were obtained instead. Likewise, reactions with only 2−5 equiv of Li_2Se produced only $Eu_2P_2Se_6$. The $[PSe_4]^{3-}$ unit could only be stabilized under strongly Lewis basic conditions.

$LiEuPSe_4$ is extremely sensitive to both air and water, decomposing in air in less than 2 s. Also, it dissolves in water upon contact, and thus, its characterization was very difficult. The only successful methods of characterization were those that allowed the use of mineral or paratone oil (optical spectra) or a nitrogen atmosphere (single-crystal X-ray diffraction). The compound forms as irregularly shaped medium-red to dark-red polyhedra-like crystals. The crystals appeared very cracked and opaque in some areas. Selecting a single crystal for data collection proved to be unsuccessful, so a twinned specimen was used instead.

Crystals of $KEuPSe_4$ were synthesized by reacting Eu, K_2Se, P_2Se_5, and Se in a 2:2:1:10 molar ratio at 495 °C for 4 days. In this case, synthesis using direct combination of the elements, at the same temperature and for the same amount of time, was also successful. However, crystals large enough for single-crystal X-ray diffraction could not be obtained using this procedure. This compound is also sensitive to air and water but not as much as $LiEuPSe_4$. $KEuPSe_4$ decomposes in air within a couple of hours and dissolves in water in about 1 min. The related compounds $KPbPSe_4$[37] and $CsPbPSe_4$ [6] can also be made by direct combination of the elements. Differential thermal analysis of $KEuPSe_4$ shows that the compound melts congruently at 817 °C.

It is indeed curious why we have not been able to obtain the Pb analogue of $LiEuPSe_4$ or the Eu analogue of $Na_{1.5}Pb_{0.75}PSe_4$.[16] However, we cannot yet rule out the existence of these compounds. Perhaps we have not yet found the conditions that favor their formation.[38]

Structure. (a) $LiEuPSe_4$. The structure of $LiEuPSe_4$ is three-dimensional and features $[PSe_4]^{3-}$ building units. Looking down the *a* axis in Figure 1, one can see the $[EuPSe_4]_n^{n-}$ framework and its small tunnels where the lithium atoms reside. The lithium atoms are four-coordinate and have an extremely distorted tetrahedral geometry (see Table 3). The average Li−Se distance is 2.95(6) Å. There are also four long Li−Se distances, two of which are 3.42(7) Å and two others of which are 3.68(8) Å. Looking down the *c* axis in Figure 2, one can see a pseudo-tetragonal arrangement with columns of P atoms running along the *b* axis, separated by parallel columns containing both Eu and Li atoms. The Eu and Li atoms alternate along the *b* and *c* axes. The Eu^{2+} centers are bonded to eight Se atoms to form a local geometry of a triangulated dodecahedron or distorted square antiprism (see Figure 3). The average Eu−Se distance is 3.191(6) Å, comparable to the Eu−Se distances in $EuSe_2$ [26] of 3.1751(7) Å. Four of the Se atoms belong to different

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(35) *SHELXTL Reference Manual*, version 5.1; Bruker Analytical X-ray Systems Inc.: Madison, WI, 1997; pp 12−15.

(36) Young, V. G., Jr. *UNTWIN*; Department of Chemistry, The University of Minnesota: Minneapolis, MN, 1997.

(37) $KPbPSe_4$ was shown to be X-ray isomorphous to $CsPbPSe_4$ with the unit cell $a = 17.423(7)$ Å, $b = 6.951(4)$ Å, and $c = 6.751(2)$ Å. Aitken, J. A.; Kanatzidis, M. G. Unpublished results.

(38) Aitken, J. A.; Kanatzidis, M. G. Work in progress.

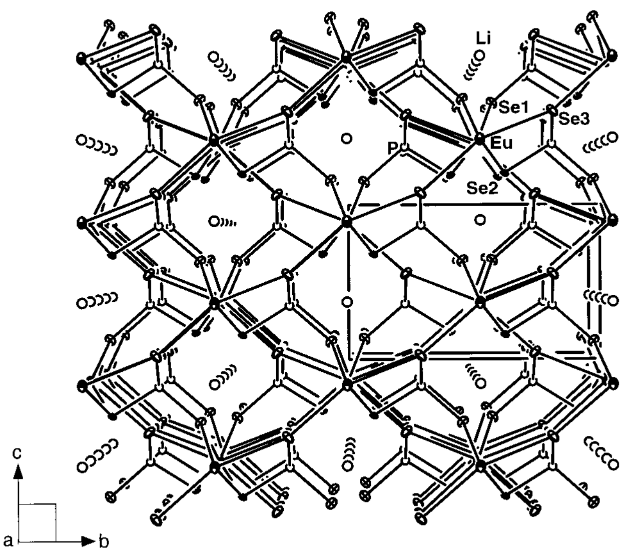

Figure 1. ORTEP representation of LiEuPSe$_4$ viewed down the *a* axis with thermal vibrational (80%) ellipsoids. This view shows the $[EuPSe_4]_n^{n-}$ framework that creates tunnels for the Li ions to reside.

Table 3. Selected Intramolecular Distances (Å) and Angles (deg) for LiEuPSe$_4$

	distance		angle
Li−Se(3)	2.72(3) × 2	Se(3)−Li−Se(3)	132(3)
Li−Se(1)	3.17(3) × 2	Se(3)−Li−Se(1)	76.8(2) × 2
		Se(3)−Li−Se(1)	130.0(3) × 2
		Se(1)−Li−Se(1)	118(2)
Li−Se (1)	3.42(7) × 2		
Li−Se (2)	3.68(8) × 2		
Li−Eu	3.21(6)		
Li−Eu	3.28(6)		
P−Se(3)	2.200(5) × 2	Se(3)−P−Se(3)	109.7(4)
P−Se(1)	2.200(8)	Se(3)−P−Se(1)	113.1(2) × 2
P−Se(2)	2.223(7)	Se(3)−P−Se(2)	107.0(2) × 2
		Se(1)−P−Se(2)	106.5(4)
Eu−Se(2)	3.119(2) × 2	Se(2)−Eu−Se(2)	65.50(6)
Eu−Se(1)	3.188(2) × 2	Se(1)−Eu−Se(1)	117.1(1)
Eu−Se(3)	3.198(2) × 2	Se(1)−Eu−Se(3)	81.27(6)
Eu−Se(3)	3.259(2) × 2	Se(2)−Eu−Se(3)	64.48(5)
		Se(1)−Eu−Se(3)	81.27(6)
		Se(3)−Eu−Se(3)	138.3(1)
		Se(2)−Eu−Se(3)	73.26(6)

Table 4. Selected Intramolecular Distances (Å) and Angles (deg) for KEuPSe$_4$

	distance		angle
K−Se(3)	3.377(5) × 2	Se(1)−K−Se(1)	88.2(9)
K−Se(3)	3.437(5) × 2	Se(3)−K−Se(3)	61.2(1)
K−Se(1)	3.442(6)	Se(3)−K−Se(3)	61.4(1)
K−Se(2)	3.544(6)	Se(3)−K−Se(3)	116.8(2)
K−Se(1)	3.610(2) × 2	Se(2)−K−Se(1)	75.09(9)
P−Se(3)	2.197(4) × 2	Se(3)−P−Se(3)	105.7(3)
P−Se(2)	2.203(6)	Se(3)−P−Se(2)	108.1(2) × 2
P−Se(1)	2.203(6)	Se(3)−P−Se(1)	111.0(2) × 2
		Se(2)−P−Se(2)	112.7(3)
Eu−Se(1)	3.088(3)	Se(2)−Eu−Se(3)	91.39(5)
Eu−Se(2)	3.143(2)	Se(1)−Eu−Se(3)	85.47(5)
Eu−Se(3)	3.151(2) × 2	Se(3)−Eu−Se(3)	66.36(6)
Eu−Se(3)	3.199(2) × 2	Se(3)−Eu−Se(3)	143.46(4)
		Se(2)−Eu−Se(3)	140.23(4)
Eu−P	3.572(6)		
Eu−Se(2)	3.6050(7) × 2		

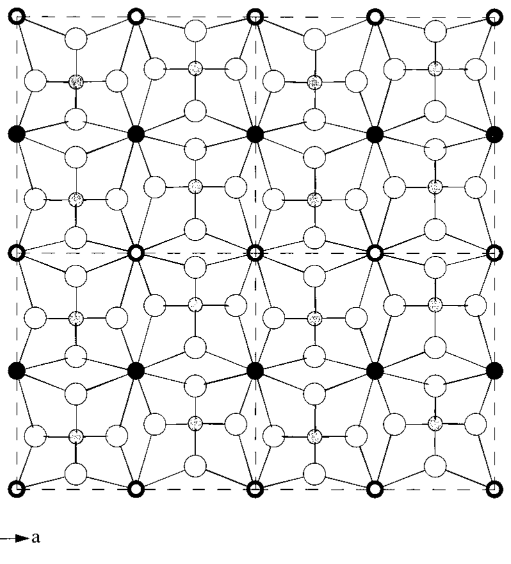

Figure 2. Structure of LiEuPSe$_4$ looking down the *c* axis. This projection shows a pseudotetragonal arrangement with columns of P atoms running along the *b* axis, separated by parallel columns containing both Eu and Li atoms. Li atoms are small, open circles. Eu atoms are black. P atoms are gray circles, and Se atoms are large, open circles.

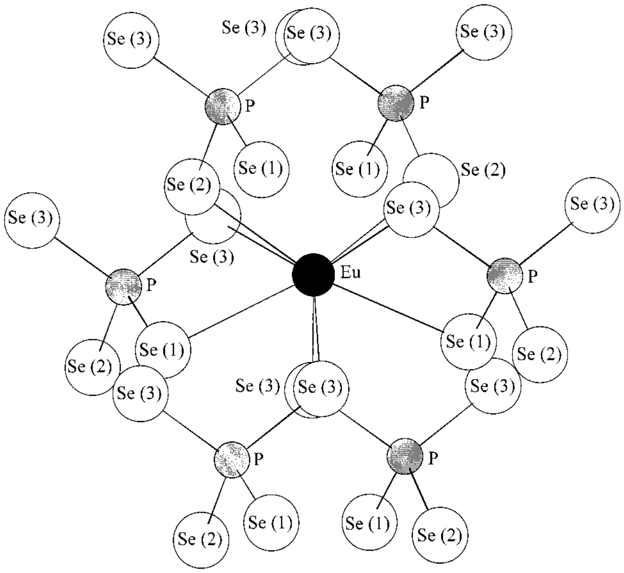

Figure 3. Extended coordination sphere of Eu in LiEuPSe$_4$.

tetrahedral units, while the other four Se atoms can be divided into two pairs each belonging to another PSe$_4$ unit. In other words the EuSe$_8$ square antiprisms share four corners with four PSe$_4$ tetrahedra and share two edges with two other tetrahedra. The EuSe$_8$ square antiprisms alone form a three-dimensional network by sharing corners in the *bc* plane, edges in the *ab* plane, and corners and edges in the *ac* plane (see Figures 4 and 5). Each Se atom is bound to one P atom and two Eu atoms. The average P−Se distance is 2.21(1) Å, which compares well to other compounds we have made that contain the PSe$_4$ unit, for example, 2.20(2) Å in CsPbPSe$_4$ [6] and 2.200(8) Å in K$_4$Eu(PSe$_4$)$_2$.[6] The Se−P−Se bond angles range from 106.5(4)° to 113.1(2)° with an average of 109.4(7)°.

It is very easy to see from Figure 5 why the structure is noncentrosymmetric. Not only the PSe$_4$ tetrahedra point in the same direction (which is often the case in noncentrosymmetric compounds that contain the PSe$_4$ unit) but also the EuSe$_8$ distorted square antiprisms all point in the same direction. Likewise, the LiSe$_4$ tetrahedra all point in the same direction,

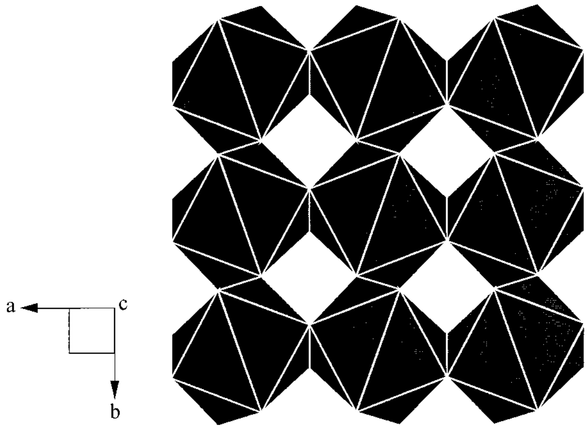

Figure 4. $EuSe_8$ triangulated dodecahedron (or distorted square antiprisms) in $LiEuPSe_4$ sharing edges in the *ab* plane.

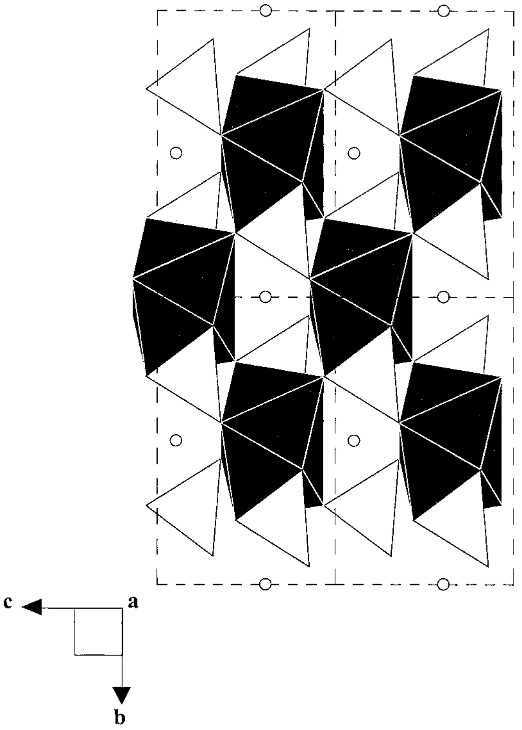

Figure 5. Polyhedral representation of $LiEuPSe_4$ looking down the *a* axis. It is easy to recognize that the structure is noncentrosymmetric because all PSe_4 tetrahedra and $EuSe_8$ square antiprisms point in the same direction. Li atoms are small, open circles. The $EuSe_8$ square antiprisms are black, and the PSe_4 tetrahedra are gray.

thus leaving no coordination polyhedra in the entire structure related by a center of inversion. If we were to consider the four shorter Li−Se distances bonding, the $LiSe_4$ tetrahedra would form chains of corner-sharing tetrahedra that would run parallel to the *a* axis.

$LiEuPSe_4$ is related to the $CaAl_2Se_4$[39] structure type in a remarkable way. $CaAl_2Se_4$ has an orthorhombic cell where $a = 6.33(1)$ Å, $b = 10.48(1)$ Å, and $c = 10.53(1)$ Å. It crystallizes in the centrosymmetric space group *Cccm* (no. 66), which is a nonisomorphic supergroup of *Ama*2. The structure is composed of $CaSe_8$ and $AlSe_4$ polyhedra. The Eu atoms of $LiEuPSe_4$ can be compared to the Ca atoms of $CaAl_2Se_4$ in that they form a similar pattern in the unit cell and have a similar coordination environment. The $CaSe_8$ polyhedra, however, are more regular square antiprisms. Both structures make tunnels down the short axis; however, in $LiEuPSe_4$ the tunnels are filled with Li atoms, whereas in $CaAl_2Se_4$ the tunnels are smaller and empty. The main difference between the two structures is the PSe_4 and $AlSe_4$ tetrahedra. In $LiEuPSe_4$ the tetrahedral units are totally separated, whereas in $CaAl_2Se_4$ they are corner-sharing to make $[Al_2Se_4]^{2-}$ chains. If every other Al atom is removed from this chain, the remaining $AlSe_4$ tetrahedra would be the same as the PSe_4 units in $LiEuPSe_4$. One can derive the $LiEuPSe_4$ structure type from that of $CaAl_2Se_4$ by doing three things. First, one would remove every other Al atom from the $[Al_2Se_4]^{2-}$ chains, making the structure noncentrosymmetric. Next, one could distort the square antiprisms of $CaSe_8$ in such a way to make them triangulated dodecahedra. Finally, one would need to insert a small cation (i.e., Li^+) that prefers tetrahedral coordination in the tunnels that run down the *c* axis. These sites are essentially interstitial sites in the structure of $CaAl_2Se_4$. In other words, one can view the structure of $LiEuPSe_4$ as a defect structure of $CaAl_2Se_4$ where the former is derived from the latter by simultaneously creating vacancies and filling interstitial sites. Thus, $LiEuPSe_4$ and $CaAl_2Se_4$ can be thought of as $LiEu\square PSe_4$ and $\square CaAlAlSe_4$, where $\square$ = vacancies. In this context, it is possible to predict other compounds on the basis of this interstitial/vacancy principle. For example, compounds of the type $LiEuMAlSe_4$ could be anticipated where M is a divalent metal with tetrahedral coordination preference such as Zn or Cd.[38]

Other compounds that can be considered somewhat related to $LiEuPSe_4$ are $LnPS_4$ (where Ln = Sc, Y, La, Ce, Pr, Nd, Sm, Gd, Tb, Er, Tm, and Yb).[40] The $LnPS_4$ structure type contains a three-dimensional network of lanthanide and sulfur atoms. The structure crystallizes in the space group $I4_1/acd$ and is composed of $[PS_4]^{3-}$ tetrahedra and LnS_8 square antiprisms. The LnS_8 square antiprisms share corners in the *ab* plane, edges and corners in the *bc* plane, and edges and corners in the *ac* plane. Each LnS_8 shares an edge with four PS_4 units.

(b) $KEuPSe_4$. The structure of $KEuPSe_4$ has two-dimensional character. Looking down the *a* axis in Figure 6, one can see layers of $[EuPSe_4]_n^{n-}$ separated by K^+ cations that have a distorted bicapped trigonal prismatic coordination. The average K−Se distance is 3.48(1) Å. The layers are composed of wedgelike $EuSe_6$ trigonal prisms and PSe_4 tetrahedral units (see Figure 7). Each Eu is connected to four PSe_4 tetrahedral units. With two of the tetrahedra it shares an edge; with the other two it shares only corners. The $EuSe_6$ trigonal prisms share rectangular edges in such a way that the trigonal faces of the prisms (i.e., the wedges) point alternately up as they form parallel chains along the *b* axis. The PSe_4 tetrahedra connect these chains along the *a* axis by sharing their edges with the rectangular faces of the trigonal prisms and the opposite edges. The average Eu−Se distance is 3.155(5) Å. The average P−Se distance is 2.20(8) Å. The Se−P−Se bond angles range from 105.7(3)° to 112.7(3)° with an average of 109.4(7)° in order to make more or less regular tetrahedra.

$KEuPSe_4$ is closely related to $CsPbPSe_4$.[6] $CsPbPSe_4$ crystallizes in the orthorhombic space group, *Pnma* (no. 62) with $a = 18.607(4)$ Å, $b = 7.096(4)$ Å, and $c = 6.612(4)$ Å. The *a* axis

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[39] Klee, W.; Schäfer, H. *Z. Naturforsch. B: Anorg. Chem., Org. Chem.* **1978**, *33* 829−833.

[40] (a) Yampol'skaya, V. V.; Serebrennikov, V. V. *Russ. J. Inorg. Chem.* **1972**, *17* (12), 1771−1772. (b) Wibbelmann, C.; Brockner, W.; Eisenmann, B.; Schäfer, H. *Z. Naturforsch.* **1984**, *39a*, 190−194. (c) Volodina, A. N.; Koubchinova, T. B.; Maximova, S. I.; Mouraviev, E. N.; Niazov, C. A.; Tchibiskova, N. I. *Zh. Neorg. Khim SSSR* **1987**, *32*, 2899−2901. (d) Le Rolland, B.; Molinié, P.; Colombet, P. *C. R. Acad. Sci., Ser. II (Paris)* **1990**, *310*, 1201−1206. (e) Le Rolland, B.; McMillan, P.; Molinié, P.; Colombet, P. *Eur. J. Solid State Inorg. Chem.* **1990**, *27*, 715−724.

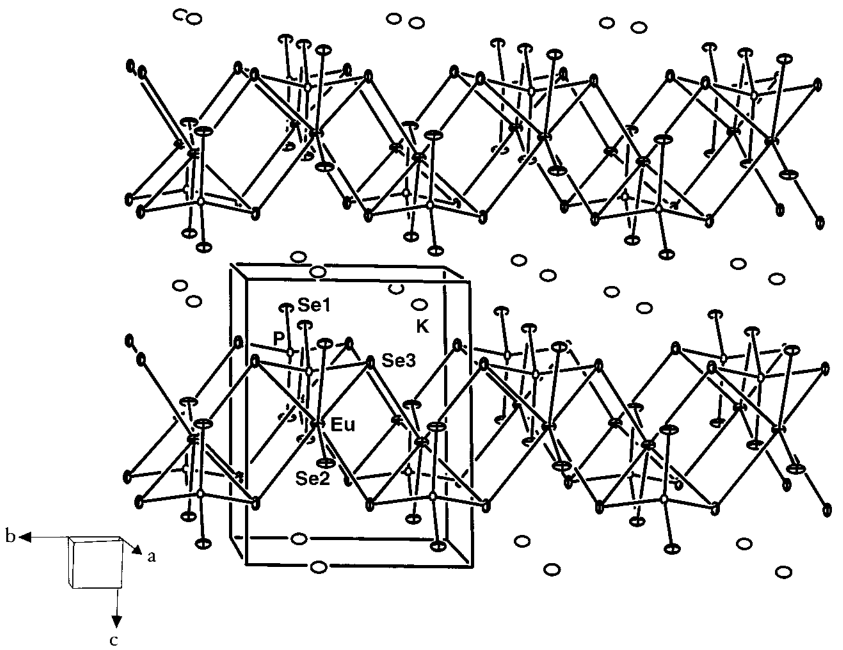

Figure 6. ORTEP representation of $KEuPSe_4$ looking down the *a* axis with thermal vibrational (80%) ellipsoids.

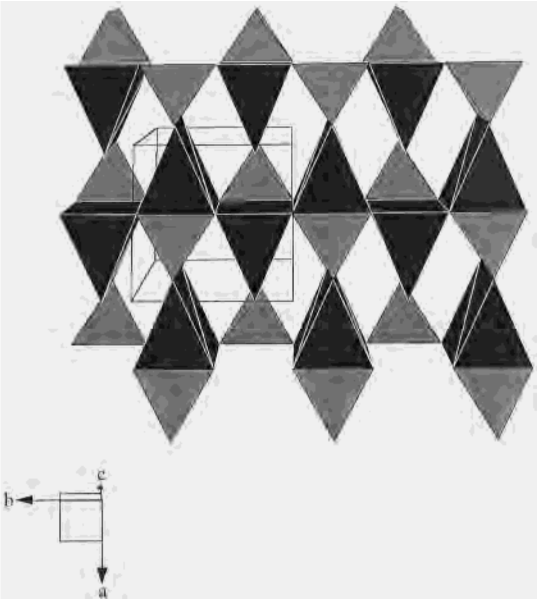

Figure 7. Polyhedral representation of $KEuPSe_4$ looking down the *c* axis. Potassium atoms have been omitted for clarity. The $EuSe_6$ trigonal prisms are shown in black, and the PSe_4 tetrahedra are displayed in gray.

in $CsPbPSe_4$ corresponds to more than twice the *c* axis of $KEuPSe_4$ (2 × 9.0436(8) Å), its *b* axis is related to the *b* axis of $KEuPSe_4$ (6.9521(6) Å), and its *c* axis can be related to the *a* axis of $KEuPSe_4$ (6.8469(6) Å). What this means is that the layer is basically the same (*bc* plane for $CsPbPSe_4$ and *ab* plane for $KEuPSe_4$). One difference between the two compounds is that in $CsPbPSe_4$ there are two layers per unit cell, and the distance between the layers is larger, of course, to accommodate the Cs^+ ions. There are two layers per unit cell in $CsPbPSe_4$ because every other layer is rotated 180° about the *a* axis. Another difference is the immediate coordination environment of the alkali metals. The Cs^+ ions in $CsPbPSe_4$ define an irregular seven-coordinate polyhedra. The P−Se distances in both compounds are nearly the same; however, in $CsPbPSe_4$ the Se−P−Se angles vary less, 107.7(3)−110.9(3)°, making more perfect tetrahedra. It is interesting that $KPbPSe_4$[37] adopts the $CsPbPSe_4$ structure type while $KEuPSe_4$ deviates slightly from this type. We can surely say that the differences in the solid-state chemistry of Pb and Eu in selenophosphate compounds are subtle.

Both the $CsPbPSe_4$ and $KEuPSe_4$ structure types are closely related to the $KLaGeS_4$ structure type, which includes the members $KLnGeQ_4$ (where Ln = La, Nd, Gd, Y; M = Si, Ge; Q = S, Se).[41] Even though these lanthanide metals have a 3+ oxidation state, while Eu bears a 2+ oxidation state, the difference in charge is compensated by the more highly charged $[GeQ_4]^{4-}$ tetrahedral units. The lattice parameters of $KLaGeS_4$ are similar to that of $KEuPSe_4$ with $a = 6.653(1)$ Å, $b = 6.643(2)$ Å, $c = 8.643(2)$ Å, and $\beta = 107.57(1)°$. This structure crystallizes in the space group $P2_1$. However, all atoms in the structure can be approximately related by a center of symmetry except those of Q(4). In this structure there are layers of $[LaGeS_4]_n^{n-}$ separated by K^+ ions. There is only one layer per unit cell as in $KEuPSe_4$. The La atoms have a larger coordination number than the Pb and Eu atoms in $CsPbPSe_4$ and $KEuPSe_4$. The La atoms are in a monocapped trigonal prism of S atoms. The capping atom, S(4), causes the structure to be noncentrosymmetric because all of the caps point in the same direction along the polar *b* axis. If this bond is ignored, the structure is very similar to $CsPbPSe_4$ and $KEuPSe_4$. The remaining six La−S bonds form a trigonal prism that is basically identical to the $PbSe_6$ or $EuSe_6$ found in $CsPbPSe_4$ and $KEuPSe_4$. We can derive the pattern of the GeS_4 tetrahedral units in the $KLaGeS_4$ structure by taking the rows of PSe_4 units, from $CsPbPSe_4$ or $KEuPSe_4$, that run parallel to the *b* axis and tilting each row alternately left and right. The coordination environment of the potassium atom is similar as well. Although the K^+ cations in $KLaGeS_4$ have been described as trigonal prismatic sites, we feel that the coordination geometry can be more accurately described as a bicapped trigonal prism where six of the K−S distances range from 3.216(1) to 3.404(2) Å and where the two others are 3.472(2) and 3.558(2) Å. This is similar to the environment of the K atom in $KEuPSe_4$. In $KLaGeSe_4$ the K atom is in an irregular seven-coordinate site, with six K−Se

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(41) Wu, P.; Ibers, J. A. *J. Solid State Chem.* **1993**, *107*, 347−355.

distances ranging from 3.342(3) to 3.508(3) Å, with the seventh distance being 3.520(3) Å. There is one other distance of 3.828(4) Å, which is too long to be considered a bond. This K environment is similar to the coordination of the Cs^+ ion found in $CsPbPSe_4$. Thus, it seems that $KLaGeS_4$ is the noncentrosymmetric cousin of $CsPbPSe_4$ and $KEuPSe_4$ mainly because of the larger coordination sphere of the La^{3+} ion.

Counterion Effect. It is apparent that a counterion effect exists in these systems. This effect is well manifested in the area of metal chalcogenide and polychalcogenide chemistry.[24,42] The counterion effect is quite predictable and can actually be exploited to direct the synthesis of solids with a desired dimensionality. In our examples these effects take place because of the large size difference in the alkali metal cations and resulting steric effects. In the presence of a smaller cation, for example, the anions have to pack closer to each other. If the cationic volume in the structure is decreasing but the anionic volume is not, this results in destabilizing repulsions. If the stoichiometry is to remain the same, the system must respond to decrease its anionic volume in order to avoid these repulsions. The anionic volume could be decreased in three different ways.[42] One is to increase the connectivity of the atoms in the anionic framework. Another is through associations of discrete molecules into larger molecules, which could be accomplished by adjustments in the conformation of the various components in the framework. A third option, which is an extension of the second, is to increase the dimensionality of the structure, e.g., one-dimensional to two-dimensional or two-dimensional to three-dimensional, etc.

While $LiEuPSe_4$, $KEuPSe_4$, $KPbPSe_4$,[37] $RbPbPSe_4$,[6] and $CsPbPSe_4$[6] have very similar formulas, there exist three different structure types among them and two different dimensionalities. The dimensionality of these structure types increases as the alkali metal cation size decreases. Thus, the $[MPSe_4]^-$ framework in $LiEuPSe_4$ is three-dimensional, whereas in $KEuPSe_4$, $KPbPSe_4$, $RbPbPSe_4$, and $CsPbPSe_4$ it is two-dimensional. In $LiEuPSe_4$ the Eu atoms are eight-coordinate, while the Eu atoms in $KEuPSe_4$ are six-coordinate, as are the Pb atoms in $KPbPSe_4$, $RbPbPSe_4$, and $CsPbPSe_4$.

When comparing $AMPSe_4$[6,37] (where A = K, Rb, Cs for M = Pb and A = K for M = Eu)[6] to $A_4M(PSe_4)_2$ (where A = Rb and Cs for M = Pb and A = K for M = Eu),[6] one can see that when the ratio of alkali metal to $[PSe_4]^{3-}$ ligands is increased, the dimensionality of the structure decreases. $A_4M(PSe_4)_2$ compounds have one-dimensional structures. In this case the cationic volume is increasing. One can view these compounds as members in a series of compounds of the type $(A_3PSe_4)_n[M_3(PSe_4)_2]_m$ where $n = 1$, $m = 1$ and where $n = 4$, $m = 1$, respectively.[6,23] $M_3(PSe_4)_2$ (where M = Pb, Eu) would be the parent members ($n = 0$, $m = 1$) of this series. These compounds are not known, but one of their sulfur analogues is $(Pb_3(PS_4)_2$[43] and has a three-dimensional structure. One can imagine dismantling the putative three-dimensional network of $M_3(PSe_4)_2$ by introducing $[PSe_4]^{3-}$ units into its structure to obtain the two-dimensional network of $APbPSe_4$. Additional introduction of $[PSe_4]^{3-}$ results in the one-dimensional $A_4Pb(PSe_4)_2$. Upon incorporation of more A_3PSe_4, one may anticipate a breakdown of the one-dimensional chains and the formulation of $A_7M(PSe_4)_3$ (where M = Pb or Eu), which would likely be a discrete molecular species.[20]

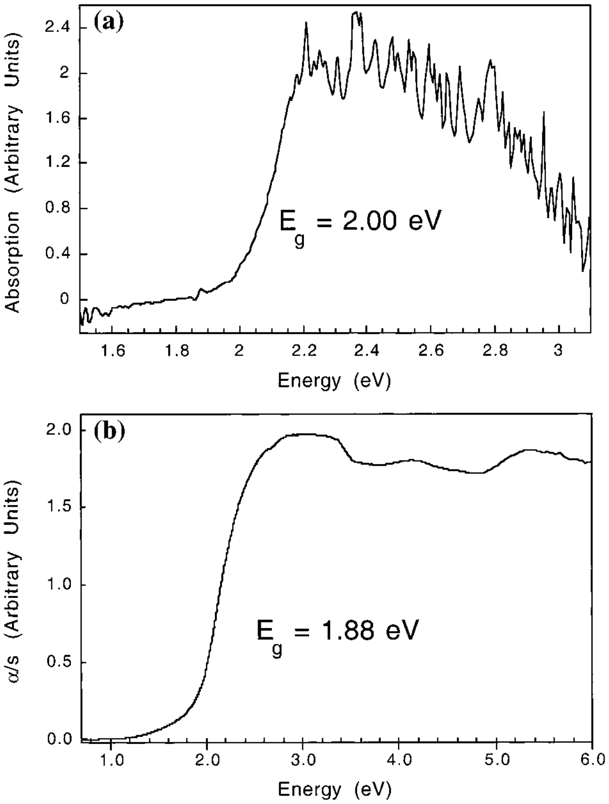

Figure 8. (a) Optical transmission spectrum converted to absorption for a single crystal of $LiEuPSe_4$. (b) Optical diffuse reflectance spectrum converted to absorption for a polycrystalline sample of $KEuPSe_4$.

Spectroscopy. The transparent crystals of $LiEuPSe_4$ were suitable for single-crystal optical transmission measurements. The crystals were protected from the air with mineral oil, which does not interfere with the measurement. Figure 8 shows that $LiEuPSe_4$ is a semiconductor with a well-defined energy gap, E_g, of 2.00 eV. Crystals of $KEuPSe_4$ were not transparent enough for single-crystal measurements, so instead, the solid-state UV/vis diffuse reflectance spectrum was obtained. $KEuPSe_4$ exhibits a sharp optical absorption of 1.88 eV (see Figure 8).

The far-IR spectra of $KEuPSe_4$ was successfully obtained. The spectrum of $LiEuPSe_4$ was not obtainable because the compound decomposes in air in less than 2 s and in this characterization method the sample could not be protected by mineral oil because it interferes with the measurement. The spectrum of $KEuPSe_4$ displays three strong absorptions at ~462, 451, and 443 cm^{-1}. These vibrations can be assigned to PSe_4 stretching modes and are diagnostic in distinguishing the tetrahedral selenophosphate ligand from others such as the ethane-like $[P_2Se_6]^{4-}$ species.[44] Also, there are three absorptions at 240, 173, and 161 cm^{-1}, which could be due to Eu−Se stretching as well as other modes associated with the $[PSe_4]^{3-}$ ligand.

Concluding Remarks

The first quaternary lithium-containing selenophosphate, $LiEuPSe_4$, was prepared using the polyselenophosphate flux method. We could not prepare $LiEuPSe_4$ from direct combination of the elements but only in a very basic $Li_2Se/P_2Se_5/Se$ flux, where the concentration of Li_2Se is high. The three-

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dimensional structure is polar, featuring the $[PSe_4]^{3-}$ tetrahedral building unit. The noncentrosymmetric $[EuPSe_4]_n^{n-}$ framework in the structure provides tunnels in which the Li ions reside in a distorted tetrahedra of Se atoms. $KEuPSe_4$ was also synthesized via the polyselenophosphate flux method but has a two-dimensional character with a structure related to that of $CsPbPSe_4$. This work is interesting for three main reasons. First, the compounds contain the harder to stabilize $[PSe_4]^{3-}$ tetrahedral unit. Often in this chemistry P^{5+} centers are unstable with respect to P^{4+} species. However, the $[PSe_4]^{3-}$ unit is becoming increasingly accessible as studies of selenophosphate systems continue. Second, the two phases are subject to the counterion effect where smaller cations favor a higher dimensionality in the structure. Third, Li was successfully incorporated in a quaternary selenophosphate for the first time. The incorporation of Li in complex multinary compounds is generally a challenging task. Furthermore, it is also important to point out that the structures of both compounds could not have been solved or acceptably refined without taking into account crystal twinning. To contrast the chemistry described here with that of the corresponding sulfur systems, further investigations in the $M/A_2S/P_2S_5/S$ systems ($M = Pb$ or Eu; $A =$ an alkali metal) are underway.[38]

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Supporting Information Available: An X-ray crystallographic file, in CIF format, containing information for both $LiEuPSe_4$ and $KEuPSe_4$. This material is available free of charge via the Internet at http://pubs.acs.org.

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