First Quaternary A–Pb–Bi–Q (A = K, Rb, Cs; Q = S, Se) Compounds: Synthesis, Structure, and Properties of α and β -CsPbBi₃Se₆, APbBi₃Se₆, (A = K, Rb), and APbBi₃S₆ (A = Rb, Cs)

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 α -CsPbBi₃Se₆ (I), β -CsPbBi₃Se₆ (II), RbPbBi₃Se₆ (III), KPbBi₃Se₆ (IV), CsPbBi₃S₆ (V), and RbPbBi₃S₆ (VI) were synthesized by the polychalcogenide flux method. α -CsPbBi₃Se₆ was obtained at 720 °C and crystallizes in the space group *Pnma* (no. 62) with a = 23.564(6) Å, b = 4.210(2) Å, c = 13.798(3) Å at room temperature. Final $R/R_w = 3.0/3.6\%$. In this compound, parallel NaCl-type Pb/Bi/Se columns with rectangularly shaped cross-sections are interconnected by edge sharing to build a 3-D tunnel framework with Cs atoms located inside the tunnels. The hexagonal plates of β -CsPbBi₃Se₆ were obtained at 400 °C and crystallize in the space group $P6_3/mmc$ (no. 194) with a = 4.213(2) Å, c = 25.22(1) Å, $\gamma =$ 120° at -100° C. Final $R/R_{\rm w} = 4.2/4.7\%$. APbBi₃Se₆ (A = Rb, K) and APbBi₃Se₆ (A = Cs, Rb) are isostructural with β -CsPbBi₃Se₆ and their hexagonal cell parameters were obtained at room temperature. The structure is composed of negatively charged Bi₂Te₃-type bilayers separated by alkali metals, which are distributed over two different crystallographic sites. The alkali metal ions are loosely packed in the interlayer space making them mobile. Topotactic ion-exchange reactions of two compounds, β -CsPbBi₃Se₆ and RbPbBi₃Se₆, were examined with LiI and NaI in the solid state and in aqueous solution. Prolonged water contact of the hexagonal compounds leads to decomposition and leaching of alkali metal and Pb²⁺ ions. Electrical conductivity and thermopower measurements for single crystals of I, II, and III show n-type semiconductor behavior with 0.6, 0.3, and 0.3 S/cm and -730, -550, and $-560 \,\mu$ V/K at room temperature, respectively. The optical band gaps of all compounds range from 0.27 to 0.89 eV. Thermal properties of the compounds are reported.

Introduction

Binary bismuth and lead chalcogenides such as Bi_2 - Te_3 , PbTe, and their solid solutions^{1,2} have been intensively studied for thermoelectric applications; however, the physical origin of their high thermoelectric figure of merit³ of these compounds remains ill-understood at the fundamental level. The most distinguished electronic feature of Bi and Pb is the 6s² lone pair of electrons, which can hybridize to give sp³d² octahedral

coordination geometry or localize to give a more distorted coordination. The expression of stereochemical activity of the 6s² lone pair of electrons influences both the structure type and electronic structure, and, consequently, all the properties of Bi and Pb compounds. Bi and Pb differ only by a single 6p electron and exhibit very similar coordination geometry and crystallographic behavior. Therefore, the structures of Pb/Bi/Q (Q = S, Se, Te) compounds exhibit various combinations of fragments which are essentially "excised" out of the structures of PbQ and Bi₂Q₃, as shown in the widely known mineral sulfo- and selenosalts: PbBi₂S₄,⁴ PbBi₄S₇,⁵ PbBi₄S₈,⁶ PbBi₆S₁₀,⁷ Pb₂Bi₂S₅,⁸ Pb₂Bi₆S₁₁,⁹ Pb₃Bi₂S₆,¹⁰

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⁽³⁾ Thermoelectric figure of merit; $ZT = (\sigma \cdot S^2/\kappa) T$, where σ is electrical conductivity; *S*, thermoelectric power; κ , thermal conductivity; and *T*, temperature.

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Pb3Bi10S18,9 Pb4Bi6S13,11 Pb6Bi2S9,12 PbBiSe2,13 PbBi2-Se₄,¹⁴ PbBi₄Se₇,¹⁴ Pb₂Bi₂Se₅,¹⁵ Pb₃Bi₄Se₉,¹⁵ Pb₈Bi₆Se₁₇,¹⁶ and Pb₉Bi₄Se₁₅.¹⁶ In these compounds, the Pb/Bi distribution in the lattice is largely undetermined.

In an effort to expand the interesting Pb/Bi/Q chemistry, we added alkali metals in the Pb/Bi/Q (Q = S, Se) system through the alkali metal polychalcogenide flux.¹⁷ This led to the first examples of quaternary A/Pb/Bi/Q (A = alkali metal) compounds. Introduction of alkali metal into the structure is expected to yield materials with more ionic character and greater structural and electronic complexity. This may lead to higher thermoelectric power based on the Mott formula.¹⁸ Furthermore, our work with ternary A/Bi/Q systems has shown that the alkali metals in the structure reside in cages or tunnels of the covalent metal-chalcogenide framework. The phonon modes associated with the "rattling" of the alkali ions in these spaces are very soft and produce a phonon damping effect which results in dramatic reduction of the solid's lattice thermal conductivity.¹⁹ This is consistent with the concept of "electron crystal phonon glass" introduced by Slack as the limiting characteristic for a superior thermoelectric.²⁰ Therefore, the role of alkali metal in a Pb/Bi/Q framework is expected to be interesting in terms of novel structural features as well as electrical and electronic properties of the resulting compounds.

Our previous work in the ternary A/Bi/Q systems can serve as a good foundation for exploration of the quaternary A/Pb/Bi/Q system, because the latter could be considered as quasi-ternary A/(Pb/Bi)/Q given the close resemblance of Bi³⁺ (Z = 83) and Pb²⁺ (Z = 82) in chemical and crystallographic terms. During the past decades, only a limited number of alkali metal group 15 chalcogenides have been studied such as $ABiQ_{2}$,²¹ $\begin{array}{l} C sBi_{3}S_{5},^{22} \ RbBi_{3}S_{5},^{23} \ Cs_{3}Bi_{7}Se_{12},^{24} \ K_{3}SbSe_{4},^{25} \ RbSb_{3}-\\ Se_{5},^{26} \ Cs_{2}Sb_{4}Se_{8},^{27} \ and \ Cs_{3}Sb_{5}Se_{9},^{28} \ Recently, \ the \ condi-$

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tions provided by the alkali metal chalcogenide flux led to the discovery of many more new compounds such as $Cs_2Sb_4S_8$ ²⁹ $CsSbS_6$ ²⁹ β - and γ -CsBiS₂³⁰ KBi₃S₅³¹ KBi_{6.33}S₁₀,¹⁹ K₂Bi₈S₁₃,¹⁹ α -³⁰ and β -K₂Bi₈Se₁₃,¹⁸ K_{2.5}Bi_{8.5}- Se_{14} , ^{18a} and BaBiTe₃, ³² however, we could find no reports of A/Pb/Bi/Q compounds.

Here we describe two classes of quaternary compounds, the three-dimensional α -CsPbBi₃Se₆ and the layered APbBi₃Q₆ (Q = Se, A = Cs, Rb, K; Q = S, A = Cs, Rb). We report the synthesis, physicochemical, spectroscopic, structural, and charge-transport characterization of these materials. The α - and β -CsPbBi₃Se₆ and RbPbBi₃Se₆ show n-type semiconducting behavior. For the layered compounds, topotactic ion exchange of large Cs⁺ and Rb⁺ ions with smaller Na⁺ and Li⁺ was successful using a new solid-state reaction method we recently reported.33

Experimental Section

Reagents. Chemicals in this work were used as obtained: (i) bismuth powder. 99.999+% purity. -100 mesh. Cerac. Milwaukee, WI; (ii) lead metal, 99.999% purity, -200 mesh, Cerac, Milwaukee, WI; (iii) selenium powder, 99.95% purity, -200 mesh, Cerac Inc., Milwaukee, WI; (iv) sulfur powder, sublimed, Spectrum Chemical Mfg. Corp., Gardena, CA; (v) potassium metal, granules, <6 mm, 99% purity, Aldrich Chemical Co., Inc., Milwaukee, WI; (vi) rubidium metal, 99.8% purity, Johnson Matthey Co., Ward Hill, MA; and (vii) cesium metal, 99.98% purity, Johnson and Matthey Co., Ward Hill, MA

Synthesis. All manipulations were carried out under a dry nitrogen atmosphere in a Vacuum Atmospheres Dri-Lab glovebox. All alkali metal selenides and sulfides were obtained by stoichiometric reactions of corresponding alkali metal and elemental chalcogen in liquid NH₃.

α-CsPbBi₃Se₆ (I). A mixture of Cs₂Se (0.248 g, 0.719 mmol), Pb (0.050 g, 0.241 mmol), Bi (0.150 g, 0.718 mmol), and Se (0.284 g, 3.597 mmol) was loaded into an alumina thimble (10 mm o.d. \times 7 mm i.d. \times 75 mm) and subsequently sealed inside a carbon-coated quartz tube (13 mm o.d. \times 11 mm i.d.) at a residual pressure of $< 10^{-4}$ Torr. The mixture was raised to 720 °C over 24 h and kept there for 6 days, followed by slow cooling to 200 °C at a rate of -4 °C/h and then to 50 °C in 6 h. Black needles of $\alpha\text{-CsPbBi}_3\text{Se}_6$ were obtained in quantitative yield after removing the Cs₂Se_x flux with dimethylformamide (DMF) and washing with diethyl ether. A quantitative microprobe analysis with a SEM/EDS (scanning electron microscope/ energy dispersive spectroscopy) was performed on several crystals to give an average ratio of Cs(Pb/Bi)_{3.6}Se_{6.5}.

β-CsPbBi₃Se₆ (II). Method A. A mixture of Cs₂Se (0.495 g, 1.436 mmol), Pb (0.050 g, 0.241 mmol), Bi (0.150 g, 0.718 mmol), and Se (0.304 g, 3.850 mmol) was loaded into a Pyrex tube (9 mm o.d. \times 7 mm i.d.) and subsequently flame-sealed at a residual pressure of $< 10^{-3}$ Torr. The mixture was heated from room temperature to 400 °C over 12 h and kept there for

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Method B. A mixture of Cs₂Se (0.165 g, 0.479 mmol), Pb (0.050 g, 0.241 mmol), Bi (0.150 g, 0.718 mmol), and Se (0.151 g, 1.912 mmol) was heated to 720 °C for 6 days under the same conditions as in the preparation of α -CsPbBi₃Se₆. SEM/EDS analysis was carried out on several crystals obtained from both methods to give an average ratio of Cs(Pb/Bi)_{4.0}Se_{5.8}.

RbPbBi₃Se₆ (**III**). Thin black hexagonal plates of RbPbBi₃-Se₆ were obtained in quantitative yield by using Rb₂Se (0.359 g, 1.437 mmol) in method A or Rb₂Se (0.120 g, 0.480 mmol) in method B at the same reaction conditions as above. SEM/EDS analysis on several crystals showed an average ratio of Rb-(Pb/Bi)_{4.9}Se_{6.7}.

KPbBi₃Se₆ (IV). K₂Se (0.076 g, 0.484 mmol), Pb (0.050 g, 0.241 mmol), Bi (0.150 g, 0.718 mmol), and Se (0.151 g, 1.912 mmol) was thoroughly mixed and heated to 720 °C for 6 days in an alumina thimble as above. Thin metallic black plates of KPbBi₃Se₆ were obtained quantitatively by isolation in DMF. SEM/EDS analysis on several crystals showed an average ratio of K(Pb/Bi)_{4.2}Se_{5.9}.

 $CsPbBi_3S_6$ (V). A mixture of Cs₂S (0.084 g, 0.282 mmol), Pb (0.116 g, 0.560 mmol), Bi₂S₃ (0.433 g, 0.842 mmol), and S (0.020 g, 0.623 mmol) was transferred to a carbon coated quartz tube (9 mm o.d. x 7 mm i.d.) and flame-sealed under high vacuum (>10⁻⁴ Torr). The mixture was heated for 6 days at 850 °C and cooled to 500 °C at 5 °C/h and then to 50 °C in 10 h. A big chunk made up of big shiny gray-metallic plates was isolated by washing with water, methanol, and ether.

 $RbPbBi_3S_6$ (VI). A mixture of Rb_2S (0.040 g, 0.197 mmol), Pb (0.082 g, 0.395 mmol), Bi (0.246 g, 1.177 mmol), and S (0.070 g, 2.183 mmol) was transferred to a carbon-coated quartz tube and flame-sealed as above. The mixture was heated for 5 days at 800 °C and cooled to 500 °C at 10 °C/h and then to 50 °C in 10 h. A big chunk made up of big shiny gray-metallic plates was isolated as above.

Solid-State Ion-Exchange Reactions. A mixture of 0.1 g of APbBi₃Se₆ (A = Cs, Rb) and 1.5 g of LiI or NaI was ground finely inside a N₂-filled glovebox. The mixture was loaded into a die of ~1.3 cm in diameter and pressed into a pellet at a pressure of 6.5 metric tons. The pellet was placed in a Pyrex tube and sealed under vacuum (~10⁻³ Torr) and then heated to 110 °C for 10 days. After reaction the product was washed thoroughly with distilled water or methanol to remove the excess alkali metal iodide matrix.

The ion-exchanged products were examined by powder XRD for qualitative analysis. Ion exchange was assessed by SEM/ EDS on the basis of the final elemental ratio of Cs/Se in the sample.

Physical Measurements. *Electron Microscopy.* Quantitative microprobe analyses of the compound were performed with a JEOL JSM-35C scanning electron microscope (SEM) equipped with a Tracor Northern energy dispersive spectroscopy (EDS) detector. A good quantification of Pb and Bi was not possible because their characteristic X-ray fluorescence peaks (both Ma and La line) are located too closely in energy. For APbBi₃S₆, a quantitative analysis was not possible by EDS because of the overlap of Pb (Ma) and S (Ka) peaks in addition to the close proximity of the Pb and Bi peaks. Data were acquired using an accelerating voltage of 20 kV and a 1-min accumulation time.

Differential Thermal Analysis. Differential thermal analysis (DTA) was performed with a computer-controlled Shimadzu DTA-50 thermal analyzer. The ground single crystals (~20 mg total mass) were sealed in quartz ampules under vacuum. A quartz ampule containing alumina of equal mass was sealed and placed on the reference side of the detector. Typically, the samples were heated to the desired temperature at 10 °C/min and then isothermed for 2 min followed by cooling at 10 °C/min to 100 °C and finally by rapid cooling to room temperature. The reported DTA temperature is the peak temperature. The DTA sample was examined by powder X-ray diffraction after the experiment.

Infrared Spectroscopy. Diffuse reflectance measurements were made on the finely ground sample at room temperature. The spectrum was recorded in the infrared region (6000-400 cm⁻¹) with the use of a Nicolet MAGNA-IR 750 spectrometer equipped with a collector diffuse reflectance accessory from Spectra-Tech. Inc. Absorption (α/S) data were calculated from the reflectance data using the Kubelka–Munk function:³⁴ α/S $= (1-R)^2/2R$, where R is the reflectance at a given wavenumber, α is the absorption coefficient, and *S* is the scattering coefficient. The scattering coefficient has been shown to be practically wavenumber independent for particles larger than 5 μ m, which is smaller than the particle size of the samples used here. The band gap was determined as the intersection point between the energy axis at the absorption offset and the line extrapolated from the linear portion of the absorption edge in a α/S vs E (eV) plot.

Solid-State UV/Vis Spectroscopy. Optical diffuse reflectance measurements were made at room temperature with a Shimadzu UV-3101 PC double-beam, double-monochromator spectrophotometer operating in the 200-2500-nm region. The instrument was equipped with an integrating sphere and controlled by a personal computer. The digitized spectra were processed using the Kaleidagraph software program. BaSO₄ powder was used as reference (100% reflectance). Absorption data were calculated from the reflectance data using the Kubelka–Munk function as above.

Charge-Transport Measurements. Direct current (dc) electric conductivity and thermopower measurements were made on single crystals of the compounds. Conductivity measurements were performed in the usual four-probe geometry with 60- and 25- μ m gold wires used for the current and voltage electrodes, respectively. Measurements of the sample cross-sectional area and voltage probe separation were made with a calibrated binocular microscope. Conductivity data were obtained with the computer-automated system described elsewhere. $^{\rm 30,35}$ Thermoelectric power measurements were made by using a slow AC technique^{30,36} with 60- μ m gold wires serving to support and conduct heat to the sample, as well as to measure the voltage across the sample resulting from the applied temperature gradient. In both measurements, the gold electrodes were held in place on the sample with a conductive gold paste.

Conductivity specimens were mounted on interchangeable sample holders, and thermopower specimens were mounted on a fixed sample holder/differential heater. Mounted samples were placed under vacuum (10^{-3} Torr) and heated to room temperature for 2-4 h to cure the gold contacts. For a variable-temperature run, data (conductivity or thermopower) were acquired during both sample cooling and warming to check reversibility. The temperature drift rate during an experiment was kept below 1 K/min. Typically, three to four separate variable-temperature runs were carried out for each sample to ensure reproducibility and stability. At a given temperature, reproducibility was within $\pm 5\%$.

Crystallography. All compounds were examined by X-ray powder diffraction. Accurate d_{hkl} spacings (Å) were obtained from the powder patterns recorded on a Rigaku Rotaflex powder X-ray diffractometer with Ni-filtered Cu K α radiation operating at 45 kV and 100 mA. The data were collected at a rate of 1.0°/min. To assess phase purity, X-ray diffraction patterns of all compounds obtained were compared to those calculated from single-crystal data using CERIUS2 software,³⁷ see Tables 1 and 2. The unit cell parameters of all compounds were obtained by a Rigaku AFC6S four-circle diffractometer.

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Table 1. Calculated and Observed X-ray Powder Diffraction Pattern of α-CsPbBi₃Se₆

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h	k	1	d_{cald} (Å)	$d_{\rm obsd}$ (Å)	$I_{\rm obsd}/I_0$ (%)
1	0	1	11.91	11.79	100
2	0	1	8.96	8.90	5.14
0	0	2	6.90	6.85	28.96
4	0	2	4.48	4.46	12.87
2	0	3	4.28	4.26	39.48
3	0	3	3.97	3.95	54.27
5	0	2	3.89	3.88	9.70
4	0	3	3.63	3.61	8.26
6	0	2	3.413	3.398	10.09
2	0	4	3.311	3.299	12.97
7	0	1	3.270	3.259	20.80
1	1	3	3.079	3.067	18.16
7	0	2	3.025	3.013	5.14
2	1	3	3.003	2.992	10.33
8	0	1	2.881	2.871	23.39
2	0	5	2.687	2.679	18.59
2	1	4	2.602	2.591	5.04
7	1	3	2.283	2.289	4.90
6	0	5	2.258	2.252	43.85
6	1	4	2.207	2.202	24.26
9	1	2	2.116	2.111	4.18
7	1	4	2.091	2.081	7.93
1	1	6	2.011	2.062	6.82
6	1	5	1.990	1.981	5.43
10	1	2	1.971	1.961	6.72
9	1	4	1.869	1.865	15.61
5	0	7	1.819	1.815	12.25
10	0	5	1.792	1.788	4.32

Table 2. Calculated and Observed X-ray Powder Diffraction Pattern of β-CsPbBi₃Se₆

h	k	1	d_{cald} (Å) ^a	d _{obsd} (Å)	$I_{\rm obsd}/I_0$ (%)
0	0	2	12.62	12.82	100
0	0	4	6.31	6.37	9.49
0	0	6	4.21	4.24	34.18
1	0	0	3.64	3.66	3.76
1	0	3	3.340	3.358	7.84
1	0	4	3.152	3.169	7.92
1	0	5	2.952	2.969	16.93
1	0	6	2.752	2.766	4.86
1	0	8	2.384	2.398	3.68
1	0	9	2.221	2.234	11.13
1	1	0	2.101	2.115	10.74
1	0	11	1.941	1.951	5.57
1	1	6	1.880	1.886	1.41
2	0	1	1.803	1.814	6.88
2	0	5	1.712	1.719	1.58
1	0	14	1.615	1.623	1.58
2	0	8	1.576	1.586	1.74
2	0	9	1.526	1.534	1.88
1	0	17	1.375	1.381	1.61
1	1	14	1.368	1.374	2.21

^a d spacings were calculated on the basis of the cell parameters obtained at 173 K.

The intensities of three standard reflections were checked every 150 reflections to monitor crystal and instrument stability during single-crystal X-ray data collection. No significant decay was observed during the data collection period. The structures of all compounds were solved by direct methods using the SHELXS-86³⁸ software program. After empirical absorption corrections based on ψ scans, refinements with fullmatrix least-squares techniques and Fourier synthesis calculations were carried out on a VAX station 3100/76 computer using TEXSAN package of crystallographic program of the Molecular Structure Corp.³⁹ With the X-ray wavelength used, Pb and Bi scatter almost identically and so it is not possible

to distinguish the two elements. Therefore, the refinements were done with Bi on all relevant metal sites. After isotropic refinement of all atoms, a DIFABS correction was applied as recommended.⁴⁰ All atoms were refined anisotropically. Table 3 shows the crystal data and details of the structure analysis.

Structure Solution of α-CsPbBi₃Se₆. A single crystal of α -CsPbBi₃Se₆ with dimensions 0.29 \times 0.03 \times 0.01 mm was mounted on the tip of a glass fiber. The crystallographic data were collected at room temperature on a Rigaku AFC6S four circle automated diffractometer equipped with a graphitecrystal monochromator. The unit cell parameters were determined from a least-squares refinement using the 2θ , ω , χ , and ϕ angles of 20 carefully machine-centered reflections in the 6 $\leq 2\theta \leq 25^{\circ}$ range. The data were collected with the $\theta/2\theta$ scan technique.

Three high-density peaks were easily found to be heavy metals (Bi and/or Pb) after application of absorption correction based on ψ scans. The assignments of these sites were attempted with various possible combinations of Bi and Pb atoms (including mixed occupancy) but no apparent difference was observed on temperature factors and R/R_w values. Therefore, we tentatively put Bi atoms on all possible Pb/Bi sites and proceeded with the refinements. The fractional coordinates and temperature factors (\boldsymbol{B}_{eq}) of all atoms with estimated standard deviations are given in Table 4.

Structure Solution of β **-CsPbBi₃Se**₆. A single crystal with dimensions $0.32 \times 0.25 \times 0.02$ mm was mounted on a glass fiber and its crystallographic data were collected at -100 °C on a Rigaku AFC6S diffractometer by the same procedure as above. Intensity data were collected using the ω scan mode. The unit cell parameters were determined from a least-squares refinement using the 2θ angles of 17 carefully centered reflections in the $8 \le 2\theta \le 28^{\circ}$ range. An empirical absorption correction based on ψ scans of three reflections with $\chi \approx 90^{\circ}$ was applied to the data.

One heavy metal (Pb/Bi) atom and two Se atoms were found on mirror planes (3*m* and $\bar{3}m$) in the space group $P6_3/mmc$. After the first least-squares refinement, there were two independent high electron density peaks (40.39 and 26.32 e/Å³) located on two different $\overline{6}m2$ crystallographic sites. These two peaks were more than 3.5 Å apart from neighboring Se atoms and 2.45 Å apart from each other, and were assigned as disordered Cs atoms (Cs(1) and Cs(2)). Subsequent refinement gave the occupancies and temperature factors of 0.0103/0.501 Å² for Cs(1) and 0.0339/5.134 Å² for Cs(2) ($R/R_w = 14.5/17.9\%$). The total occupancy possible for each 6m2 crystallographic site is 0.0833 and the total occupancy of the Cs(1) and Cs(2) atoms was 0.0442. This suggested that the Cs atoms occupy two sites with half-occupancy (0.0417). At this stage, estimation of the composition based on total occupancies of Se atoms and Cs atoms, SEM/EDS results, and electroneutrality of the compound could be made to be Cs_{0.5}Pb_{0.5}Bi_{1.5}Se₃. Of course the location of Pb and Bi atoms cannot be crystallographically distinguished. Therefore, the total occupancy of the two disordered Cs atoms was fixed to 0.0417 which corresponds to a quarter occupancy of the Bi atom site (total possible occupancy of the Bi atom site is 0.1667), $(R/R_w = 14.3/$ 17.2%). A DIFABS correction was applied to the isotropically refined data, $(R/R_w = 8.2/10.5\%)$ as above. All reflections were averaged and successive refinements, taking into account this model, resulted in reasonable occupancies and temperature factors which were 0.0163/1.616 Å² for Cs(1), 0.0254/3.142 Å² for Cs(2), $(R/R_w = 5.2/5.7)$. Finally, all atoms were anisotropically refined, (final $R/R_{\rm w} = 4.2/4.7\%$, GOF = 1.85). The fractional atomic coordinates and temperature factors (B_{eq}) of all atoms with estimated standard deviations are given in Table 5.

Structure Solution of CsPbBi₃S₆. The crystal was mounted on a glass fiber. Intensity data were collected at room temperature on a Rigaku AFC6S diffractometer by the same procedure as above. Intensity data were collected using the ω scan mode. An empirical absorption correction based on ψ

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^{5.0;} Molecular Structure Corporation: The Woodlands, TX, 1989.

Table 3. Summary of Crystallographic Data and Structural Analysis for α -CsPbBi₃Se₆, β -CsPbBi₃Se₆, and CsPbBi₃Se₆

formula	α -CsPbBi ₃ Se ₆	β -CsPbBi ₃ Se ₆	CsPbBi ₃ S ₆
formula weight	1440.81	1440.81	1159.41
crystal habit	black needle	black plate	black plate
crystal size, mm ³	0.29 imes 0.03 imes 0.01	0.32 imes 0.25 imes 0.02	0.50 imes 0.35 imes 0.02
space group	<i>Pnma</i> (no. 62)	<i>P</i> 6 ₃ / <i>mmc</i> (no. 194)	<i>P</i> 6 ₃ / <i>mmc</i> (no. 194)
a, Å	23.564(6)	4.213(3)	4.074(2)
b, Å	4.210(2)	4.213(3)	4.074(2)
<i>c</i> , Å	13.798(3)	25.22(1)	24.549(5)
γ , deg	90	120	120
$Z; V, Å^3$	4; 1369(1)	1; 387.8(3)	1; 352.8(3)
$D_{\rm calc},{ m gcm^{-3}}$	6.991	6.169	5.457
Т, К	298	173	298
λ(Mo Kα), Å	0.71069	0.71069	0.71069
μ (Mo K _{α}), cm ⁻¹	690.76	609.55	525.27
scan mode	$\theta/2\theta$	ω	ω
$2\theta_{\max}$, deg	50.0	49.9	59.8
total data measd	1467	1347	2420
total unique data	1467	206	290
data with $I > 3\sigma(I)$	952	129	177
no. of variables	66	14	14
final R^a/R_w^b , %	3.0/3.6	4.2/4.7	8.9/10.1
goodness of fit	1.17	1.84	3.09

^a $R = \sum ||F_0| - |F_c|| / \sum |F_0|$. ^b $R_w = \{\sum w(|F_0| - |F_c|)^2 / \sum w |F_0|^2\}^{1/2}$.

Table 4. Fractional Atomic Coordinates and Equivalent Atomic Displacement Parameter (Beq) Values for α-CsPbBi₃Se₆ with Estimated Standard Deviations in Parentheses

atom	Х	У	Ζ	$oldsymbol{B}_{\mathrm{eq}}$, $^{a}\mathrm{\AA}^{2}$
M(1)	0.07536(4)	1/4	0.04651(7)	1.44(4)
M(2)	0.02500(4)	$1/_{4}$	-0.27388(7)	1.44(4)
M(3)	0.17258(4)	$-1/_{4}$	-0.1669	1.60(4)
M(4)	0.21763(4)	-1/4	0.15266(8)	2.07(5)
Cs(1)	-0.13169(7)	$1/_{4}$	-0.4620(1)	2.33(8)
Se(1)	-0.0458(1)	$^{1}/_{4}$	0.1026(2)	1.3(1)
Se(2)	0.0962(1)	-1/4	0.1866(2)	1.4(1)
Se(3)	0.0006(1)	$1/_{4}$	-0.6010(2)	1.6(1)
Se(4)	0.1469(1)	$1/_{4}$	-0.3137(2)	1.5(1)
Se(5)	0.1946(1)	$1/_{4}$	-0.0191(2)	1.4(1)
Se(6)	0.2129(1)	$^{1}/_{4}$	0.2940(2)	1.5(1)

^{*a*} Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $B_{eq} = (8\pi^2/3)[a^2B_{11} + b^2B_{22} + c^2B_{33} + ab(\cos\gamma)B_{12} + ac(\cos\beta)B_{13} + bc(\cos\alpha)B_{23}]$. The anisotropic temperature factor expression is $\exp[-2\pi^2(B_{11}a^{*2}h^2 + ... + 2B_{12}a^*b^*hk + ...)]$.

Table 5. Fractional Atomic Coordinates and Equivalent Atomic Displacement Parameter (B_{eq}) Values for β -CsPbBi₃Se₆ (Top) and CsPbBi₃S₆ (Bottom) with Estimated Standard Deviations in Parentheses

atom	X	у	Z	B_{eq} , Å ²	occupancy
			β-CsPbBi ₃ Se ₆		
M(1)	$1/_{3}$	$^{2}/_{3}$	0.42490(7)	1.08(5)	1
Cs(1)	$1/_{3}$	$^{2}/_{3}$	$^{1}/_{4}$	1.8(6)	0.20
Cs(2)	0	0	$1/_{4}$	3.1(5)	0.30
Se(1)	$^{2}/_{3}$	$1/_{3}$	0.3618(2)	1.4(1)	1
Se(2)	0	0	1/2	1.1(2)	1
			CsPbBi ₃ S ₆		
M(1)	$^{2}/_{3}$	$1/_{3}$	0.4251(1)	1.69(3)	1
Cs(1)	2/3	$1/_{3}$	$1/_{4}$	7.0(7)	0.21
Cs(2)	0	0	$3/_{4}$	6.0(4)	0.29
S(1)	$^{2}/_{3}$	$1/_{3}$	0.6359(8)	2.3(2)	1
S(2)	Ő	0	1/2	2.0(3)	1

scans was applied to the data, followed by a DIFABS correction to the isotropically refined data. One bismuth atom and four "sulfur" atoms were located. Two of the "sulfur" atoms were found sitting between the Bi_2Te_3 -type layers at a distance of 2.35 Å from each other. They were subsequently assigned as Cs atoms and their occupancies were refined. Cs(1) was 26% occupied while Cs(2) was 34% occupied. Since SEM/EDS analysis showed the presence of Cs, Pb, Bi, and S atoms, the compound must have, for charge balancing reasons, the formula $Cs_{0.5}Pb_{0.5}Bi_{1.5}S_3$. This formula indicates that the total Cs occupancy should be 50% while the site assigned as Bi must actually contain 75% Bi and 25% Pb. The sum of the occupancies of the Cs atoms was slightly higher than 50%, and it was constrained to be equal to 0.0417, which corresponds to a 50% total occupancy of the Cs atoms. All atoms were refined anisotropically ($R/R_w = 11.0/13.5\%$). Averaging the data improved the *R* values ($R/R_w = 8.9/10.1\%$). Tables 3 and 5 show the summary of crystallographic data collected and the fractional atomic coordinates of CsPbBi₃S₆.

Results and Discussion

Synthesis, Thermal Analysis, and Spectroscopy. The compounds α -CsPbBi₃Se₆ and β -CsPbBi₃Se₆ were found to form in a relatively wide range of reaction temperatures (400-750 °C). Our investigation on the Cs/Pb/Bi/Se system in flux conditions suggests that the basicity of Cs_2Se_x flux critically controls the ratio of α to β -form. The β -form seems to be the more stable phase in basic conditions at high temperatures (>700 °C) and was obtained pure from a molar ratio 2/1/3/8 of Cs₂Se/ Pb/Bi/Se at 720 °C. This compound can also be formed at low temperature (<550 °C) only if the basicity of Cs₂-Se_x flux is high enough. On the other hand, α -CsPbBi₃-Se₆ is formed as a major product in a less basic flux at high temperature. The optimized conditions for the synthesis of pure α -phase were found to be the molar ratio 2-3/1/3/15-20 of Cs₂Se, Pb, Bi, and Se at 720 °C. The stoichiometric combination reaction of Cs₂Se/Pb/ Bi/Se at 720 °C for 5 days gave a mixture of α - and β -form in which the latter was a minor product. Heating β -CsPbBi₃Se₆ at 480 °C leads to the α -form in 2 days, which suggests that the α -form is the most thermodynamically stable phase.

In the Rb₂Se/Pb/Bi/Se system, we found that the conditions to form RbPbBi₃Se₆ are much less dependent on the reaction temperature and basicity of Rb₂Se_x flux than those discussed above. The RbPbBi₃Se₆, which is isostructural to β -CsPbBi₃Se₆, was the only quaternary compound formed in a wide range of temperature and basicity. On the other hand, KPbBi₃Se₆ could be found only from high-temperature reactions (>700 °C). Stoichiometric combination reactions at 720 °C also produced the Rb and K compounds with a small amount of



Figure 1. Two projections of the structure of α -CsPbBi₃Se₆ viewed down the *b* axis. (a) A NaCl-type galena fragment is highlighted by shaded areas. Open circles correspond Se atoms. Part b shows a polyhedral representation of the structure of α -CsPbBi₃Se₆.

unknown black powdery impurities. Annealing these two compounds at 540 °C for 10 days led to the growth of a new phase with a needle morphology on the surface of the parent hexagonal crystals. This new phase turned out to be a new quaternary compound, $APb_4Bi_7Se_{15}$ (A = Rb, K).⁴¹

APbBi₃S₆ (A = Rb, Cs) was synthesized by reacting A₂S/Pb/Bi/S in 0.5/1/3/6 ratio. The reactions to prepare the K analogue, KPbBi₃S₆, were attempted at various temperatures but the isostructural phase was not formed. Instead, a new quaternary phase K_xPb_{4-2x}-Bi_{4+x}S₁₀, identified to be isostructural with cosalite Pb₂-Bi₂S₅,⁸ and KBi_{6.33}S₁₀¹⁹ were obtained.

The thermally stable phase, α -CsPbBi₃Se₆, melts congruently at 711 °C. The hexagonal phases melt at 691 (β -CsPbBi₃Se₆), 695 (RbPbBi₃Se₆), 705 (KPbBi₃Se₆), 726 (CsPbBi₃S₆), and 739 °C (RbPbBi₃S₆), respectively. These compounds did not show any sign of decomposition or phase transformation in DTA.



Figure 2. Projection of the structure of galenobismutite (PbBi₂S₄) viewed down the *b* axis. NaCl-type fragments are highlighted by shaded areas. Open circles correspond S atoms.

Structure Description. α -*CsPbBi*₃*Se*₆. This compound has a three-dimensional framework with onedimensional tunnels formed by edge-sharing NaCl-type $[PbBi_3Se_6]_n$ parallelepiped rods running along *b* axis. The cross section dimensions of these rectangular rods are $\frac{3}{2}$ by $\frac{3}{2}$ metal octahedra. Cs atoms reside inside the tunnels, as illustrated in Figure 1. The bilayered NaCl-type slab called the galena fragment, see Figure 2, is commonly used as an archetype building unit in the description of the structural characteristics of sulfosalts. The galena-type [PbBi₃Se₆]_n block in α-CsPbBi₃-Se₆ has a similar cross-section to that of galenobismutite (PbBi₂S₄).⁴ The Pb and Bi atoms in α -CsPbBi₃Se₆ possess octahedral coordination geometry, while those atoms in galenobismutite have more distorted octahedral and seven-coordinate geometry. This could be due to the greater size of Se over S, which tends to produce a more regular geometry and lower coordination number. This effect becomes obvious in going from Pb/Bi/S to Pb/Bi/S/Se and Pb/Bi/Te systems in which Pb and Bi atoms show more regular octahedral coordination with the heavier chalcogen.¹⁶

The distinction between Pb and Bi atoms in Pb/Bi mixed structures is still controversial due to their chemical resemblance but attempts to distinguish these metal atoms have been made in many sulfosalts based on their structural characteristics (bond length, angle, and coordination configuration).⁴² Galenobismutite is a typical example, demonstrating that site assignments by the statistical analysis of bond lengths^{4a, 43} of the Pb/ Bi coordination polyhedra comply with the experimental results.⁴⁴ On the basis of the Pb-S bond lengths found in sulfosalts, the Pb atom in Figure 2 was assigned to have a capped trigonal prismatic coordination to S atoms apart from 2.85 to 3.21 Å. The other two Bi atoms are in an octahedron and a capped trigonal prism with distances ranging from 2.63 to 3.12 Å and from 2.78 to 3.10 Å, respectively. Interestingly, we found an isostructural compound, CsBi_{3.67}Se₆,⁴⁵ in which Bi atom

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Table 6. Selected Bond Distances (Å) in α -CsPbBi₃Se₆ (Top) and β -CsPbBi₃Se₆ (Bottom) with Estimated Standard Deviations in Parentheses

α -CsPbBi ₃ Se ₆						
M(1)-Se(1)	2.957(3)	$M(2)-Se(1) \times 2$	3.206(2)			
$M(1)$ -Se(1) \times 2	3.027(2)	M(2)-Se(2)	3.099(3)			
$M(1)$ -Se(2) \times 2	2.902(2)	$M(2)-Se(3) \times 2$	2.791(2)			
M(1)-Se(5)	2.950(3)	M(2)-Se(4)	2.923(3)			
M(3)-Se(1)	3.114(3)	M(4)-Se(2)	2.897(3)			
$M(3)$ -Se(4) \times 2	2.986(2)	M(4)-Se(4)	3.224(3)			
$M(3)$ -Se(5) \times 2	2.979(2)	$M(4)$ -Se(5) \times 2	3.218(2)			
M(3)-Se(6)	2.750(3)	$M(4)$ -Se(6) \times 2	2.875(2)			
	β-CsPb	Bi ₃ Se ₆				
$M(1)$ -Se(1) \times 3	2.906(3)	$Cs(1)-Se(1) \times 6$	3.724(4)			
$M(1)$ -Se(2) \times 3	3.083(1)	$Cs(2)-Se(1) \times 6$	3.724(4)			
$Cs(1)-Cs(2) \times 3$	2.4323(9)					

Table 7. Selected Bond Angles (deg) in α -CsPbBi₃Se₆ (Top) and β -CsPbBi₃Se₆ (Bottom) with Estimated Standard Deviations in Parentheses

α -CsPbBi ₃ Se ₆						
$Se(1)-M(1)-Se(1) \times 2$	87.49(6)	Se(1)-M(2)-Se(1)	82.23(7)			
Se(1)-M(1)-Se(1)	88.28(8)	$Se(1)-M(2)-Se(2) \times 2$	81.62(6)			
$Se(1)-M(1)-Se(2) \times 2$	89.38(6)	$Se(1)-M(2)-Se(3) \times 2$	89.59(6)			
$Se(1)-M(1)-Se(2) \times 2$	89.20(6)	$Se(1)-M(2)-Se(4) \times 2$	89.33(6)			
Se(1)-M(1)-Se(5)	90.57(6)	$Se(2)-M(2)-Se(3) \times 2$	92.37(7)			
Se(2)-M(1)-Se(2)	93.15(9)	Se(3)-M(2)-Se(3)	98.10(9)			
$Se(2)-M(1)-Se(5) \times 2$	92.48(6)	$Se(3)-M(2)-Se(4) \times 2$	95.51(7)			
$Se(1)-M(3)-Se(4) \times 2$	89.96(6)	$Se(2)-M(4)-Se(5) \times 2$	87.28(6)			
$Se(1)-M(3)-Se(5) \times 2$	88.35(6)	$Se(2)-M(4)-Se(6) \times 2$	81.49(6)			
Se(4)-M(3)-Se(4)	89.81(8)	$Se(4)-M(4)-Se(5) \times 2$	105.84(6)			
$Se(4)-M(3)-Se(5) \times 2$	90.04(6)	$Se(4)-M(4)-Se(6) \times 2$	86.59(6)			
$Se(4)-M(3)-Se(6) \times 2$	93.76(6)	Se(5)-M(4)-Se(5)	81.84(8)			
Se(5)-M(3)-Se(5)	90.07(8)	$Se(5)-M(4)-Se(6) \times 2$	90.75(6)			
$Se(5){-}M(3){-}Se(6) \times 2$	87.93(6)	Se(6)-M(4)-Se(6)	94.32(9)			
	β-CsPl	bBi ₃ Se ₆				
$Se(1)-M(1)-Se(1) \times 3$	92.9(1)	$M(1)-Se(1)-M(1) \times 3$	92.9(1)			
$Se(1)-M(1)-Se(2) \times 6$	90.35(6)	$M(1)-Se(2)-M(1) \times 6$	86.20(4)			
$Se(2)-M(1)-Se(2) \times 3$	86.20(4)	$M(1)-Se(2)-M(1) \times 6$	93.80(4)			
Se(1)-M(1)-Se(2)	175.27(9)	M(1)-Se(2)-M(1)	180			

replaces the Pb atom in the quaternary α -CsPbBi₃Se₆. In the structure of CsBi_{3.67}Se₆, the Bi atom with 0.67 occupancy corresponding 2+ in charge has been successfully assigned to occupy M(4) site in Figure 1 which has the most distorted octahedral geometry. This suggests that in α -CsPbBi₃Se₆ M(4) is more likely to be a Pb atom and M(1), M(2) and M(3) to be Bi atoms. However, the disorder of Pb/Bi atoms over all metal sites in the structure cannot be ruled out.

It should be noticed that out of all metal sites the M(1) atom has the most regular MSe₆ octahedral coordination with more uniform M(1)–Se bond lengths and angles e.g., 2.902(2) to 3.027(2) Å and 87.49(6)° to 93.15(9)° for α -CsPbBi₃Se₆ (Tables 6 and 7) and 2.911(2) to 3.007(2) Å and 86.70(8)° to 92.24(8)° for CsBi_{3.67}Se₆. This highly regular BiQ₆ (Q = S, Se, Te) coordination is rare as the distorted octahedral geometry of Bi atom caused by the stereochemical expression of the 6s² lone pair of electrons is the most characteristic feature of Bi atoms in most known A/Bi/Q compounds.^{24,30,32,46} The relative regularity of the coordination geometry of this M(1) site is obvious in all three compounds, PbBi₂S₄, CsBi_{3.67}Se₆, and α -CsPbBi₃Se₆, which seems to be an essential structural motif to built the galena-type framework.⁴⁷

 β -*CsPbBi*₃*Se*₆. The structure of β -CsPbBi₃*Se*₆ is made up of hexagonal [PbBi₃Se₆]_n slabs, which are five atomic layers thick. Cs atoms are distributed between the layers. This structure can be considered as a hybrid between the Bi₂Se₃ and RbBiS₂ structure types (or intercalated Bi2Te3-type) as shown in Figure 3. MQ6 octahedra in seleno- and tellurosalts is a prevalent coordination geometry, giving rise to a rigid and wellordered M/Q framework. Sulfosalts, on the other hand, display more distorted MQ6 octahedra or high coordination geometry because of the smaller size of S atoms, consequently resulting in more elaborate and diverse structures. Substitution of a Pb²⁺ atom for a Bi³⁺ atom in 2[Bi₂Se₃] requires another cation to balance charge and the resulting rigid Bi₂Te₃-type [PbBi₃Se₆]⁻ layers accept monovalent alkali cations between them.

The structure of CsPbBi₃S₆ has the same features as β -CsPbBi₃Se₆. The cell parameters of all isostructural compounds, β -CsPbBi₃Se₆, RbPbBi₃Se₆, KPbBi₃Se₆, CsPbBi₃S₆ and RbPbBi₃S₆, are listed in Table 8.

The Cs atoms in β -CsPbBi₃Se₆ occupy, partially, two crystallographically distinct sites between the layers, see Figure 3b, both of which have trigonal prismatic Se coordination. The occupancy of the Cs^+ ions in the interlayer gallery is only one-half of the total capacity of the interlayer space for such ions. For example, in RbBiS₂,^{21d} which features CdCl₂-type BiS₂ layers, the corresponding gallery space is saturated with Rb⁺ ions. Comparably then, the charge density, per unit gallery area, is much lower in β -CsPbBi₃Se₆ than in RbBiS₂. The less than maximum filling of the galleries of β -CsPbBi₃Se₆ is reflected in the lower density (~12%) of this material compared to its α -allotrope. The latter presumably represents a fully dense atomic arrangement of the CsPbBi₃Se₆ composition. This explains why the α -form is the thermodynamically stable product. Long-range ordering of Cs atoms between the layers was probed with electron diffraction performed on crystals of β -CsPbBi₃Se₆ and CsPbBi₃S₆ using a transmission electron microscope. No evidence of a superlattice was observed.

Charge Transport and Optical Absorption Prop erties. Electrical conductivity and thermoelectric power measurements were carried out on single crystals of α and β -CsPbBi₃Se₆, and RbPbBi₃Se₆. The electrical conductivities of these materials show a typical semiconducting behavior over the temperature range studied. As shown in Figure 4, the conductivity of RbPbBi₃Se₆ is only 0.3 S/cm at room temperature and drops to 1.2 \times 10⁻⁸ S/cm at 4 K. The compounds, α - and β -CsPbBi₃-Se₆, also showed the same temperature dependence with 0.6 and 0.3 S/cm at room temperature, respectively. The room temperature thermoelectric power (Seebeck coefficients) of α - and β -CsPbBi₃Se₆ and RbPbBi₃Se₆ are very large at -730, -550, and $-560 \,\mu$ V/K, respectively, and exhibit a weak temperature dependence in the range of 200-300 K. (The variable-temperature ther-

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⁽⁴⁷⁾ We have used the EUTAX and VALENCE programs (*J. Appl. Crystallogr.* **1996**, *29*, 479–480) to perform bond valence sums, (the only difference in these two programs is that they adopt different R_0 values in the calculation) for α -CsPbBi₃Se₆. The results from both programs are also consistent with our assignment of the M(4) site as Pb atom. The results are as follows: from EUTAX, valence sums at Bi(1) = 3.168, Bi(2) = 3.139, Bi(3) = 3.242, Bi(4) = 2.721, Se(1) = 2.288, Se(2) = 2.205, Se(3) = 1.662, Se(4) = 1.812, Se(5) = 2.058, Se(6) = 2.245; from VALENCE, valence sums at Bi(1) = 2.929, Pb(1) = 2.882, Bi(2) = 2.999, Bi(3) = 2.898, Bi(4) = 2.514, Pb(4) = 2.474.



Figure 3. The layered structures of (a) β -CsPbBi₃Se₆, (c) Bi₂Se₃, and (d) RbBiS₂ viewed down the *b* axis. Open circles are chalcogen atoms. (b) The arrangement of Cs atoms in β -CsPbBi₃Se₆ viewed down *c* axis and the coordination geometry of two distinct Cs atoms. The corners of the trigonal prisms correspond to Se atoms in the layers.

Hexagonal APbBi ₃ Q ₆ Phases						
	<i>a</i> , Å	<i>c</i> , Å	γ, deg	<i>V</i> , Å ³	<i>Т</i> , К	
β-CsPbBi ₃ Se ₆	4.213(3)	25.22(1)	120	387.8(3)	173	
RbPbBi ₃ Se ₆	4.185(2)	24.985(5)	120	379.4(2)	173	
	4.179(2)	25.383(9)	120	383.8(3)	298	
KPbBi ₃ Se ₆	4.19(1)	25.10(2)	120	381.3(8)	298	
CsPbBi ₃ S ₆	4.074(2)	24.549(5)	120	352.8(3)	298	
RbPbBi ₃ S ₆	4.099(3)	23.73(1)	120	345.2(6)	298	

Table 8. Comparison of Unit Cell Parameters of

Table 9. Calculated and Observed X-ray Diffraction Pattern of Li⁺-Exchanged β -CsPbBi₃Se₆ Phases

h	k	1	d_{cald}^{a} (Å)	$d_{ m obsd}$ (Å)	$I_{\rm obsd}/{ m I}_0$ (%)
0	0	2	16.05	15.921	100
0	0	6	5.307	5.307	21
0	0	8	3.979	3.980	16
1	0	0	3.626	3.628	39
1	0	4	3.352	3.301	43
0	0	10	3.177	3.184	52
1	0	6	3.006	2.995	67

 a Calculated for the unit cell with a=4.189(2) Å and c=31.84(2) Å.

moelectric power data for a single-crystal sample of $RbPbBi_3Se_6$ is shown in Figure 5.) The negative values indicate that the materials have electrons (n-type) as the dominant charge carriers. The low conductivity and very large values of thermoelectric power and their temperature dependence are consistent with semiconducting behavior.

Indeed, the semiconducting nature of the materials could be confirmed independently with optical spectros-



Figure 4. Variable-temperature electrical conductivity data for a single-crystal sample of RbPbBi₃Se₆.

copy which provides a reliable way for the determination of band gaps in semiconductors.^{18a} The compounds, α and β -CsPbBi₃Se₆ and RbPbBi₃Se₆, show well-defined electronic transitions associated with a band gap of 0.55, 0.71, and 0.71 eV, see Figures 6 and 7. The low dimensionality and the low density of β -CsPbBi₃Se₆ and RbPbBi₃Se₆ are probably the origin of the wider band gaps of these compounds relative to α -CsPbBi₃Se₆. The sulfide compounds CsPbBi₃Se₆ and RbPbBi₃Se₆ have even



Figure 5. Variable-temperature thermoelectric power data for a single-crystal sample of RbPbBi₃Se₆.



Figure 6. Infrared absorption spectrum of α -CsPbBi₃Se₆. The semiconductor energy gap is indicated in the spectrum.

wider band gaps of 0.89 each because of the higher electronegativity of the S atom.

Surprisingly, the band gap drops substantially from 0.71 eV in β -CsPbBi₃Se₆ and RbPbBi₃Se₆ to 0.30 eV in the corresponding isostructural KPbBi₃Se₆. This is harder to explain but perhaps it is due to enhanced covalent character in the K⁺...Se interactions because of the smaller size of K⁺ ion compared to Rb⁺ and Cs⁺ ions. The relative covalent character of A–Q interactions increases as one moves from the bottom (i.e., Cs) to the top (i.e., Li) of the periodic table.

Solid-State Ion-Exchange Properties of β -CsPbBi₃-Se₆ and RbPbBi₃Se₆. Since the hexagonal compounds APbBi₃Se₆ (A = Cs, Rb) have a layered framework and low density of alkali metal ions between the layers, we examined their ability to undergo cation-exchange reactions. The ion-exchange chemistry with smaller ions, such as Li⁺ and Na⁺, was carried out using a new, low-temperature, solid-state ion-exchange route we have developed using alkali metal iodides, see eq 1.³³ In this route a compressed mixture of the material and excess alkali iodide is heated mildly (~90–120 °C) for several days. Remarkably, an ion-exchange process seems to occur at interparticle interfaces via an unknown mechanism.

$$APbBi_{3}Se_{6}(s) (A = Cs, Rb) + excess NaI(s) \xrightarrow{\Delta} NaPbBi_{3}Se_{6}(s) + AI(s) (1)$$



Energy (eV) **Figure 7.** Solid-state UV/vis spectra of (a) β -CsPbBi₃Se₆ and (b) CsPbBi₃S₆.



Figure 8. Comparison of X-ray diffraction patterns of (a) pristine β -CsPbBi₃Se₆ and the products obtained from the solid-state ion-exchange reactions of β -CsPbBi₃Se₆ with (b) NaI and (c) LiI.

From powder XRD patterns (Figure 8) and SEM/EDS analyses a substantial amount of cations was observed to have been exchanged. The Na⁺-exchanged products display partial exchange as indicated by the two interlayer spacings, 12.17 and 12.78 Å, of (002) planes (11.75 and 12.42 Å for RbPbBi₃Se₆) observed by X-ray diffraction. The higher interlayer spacings at 12.78 and 12.42 Å are those of the pristine starting materials. The Na⁺exchanged part of the sample shows an interlayer contraction, consistent with the smaller size of this ion. The simultaneous presence of pristine and ion-exchanged product indicates a heterogeneous ion-exchange mechanism in which the process begins at the outer edges of the hexagonal platelets and proceeds toward the center. This would involve a moving phase boundary between the NaPbBi₃Se₆ and CsPbBi₃Se₆ regions and no intermediate Na_{1-x}Cs_xPbBi₃Se₆ phases. This argument is supported by spatially resolved microprobe EDS analyses of the corresponding crystals.

On the other hand, Li⁺-exchange reactions on both compounds appear to be nearly completed at the same period of reaction time as used for Na⁺ exchange (10 days) probably because of the higher mobility of the Li⁺ ion. In fact, very long reaction time (>5 days) gives a product with poor crystallinity. Quantitative SEM/EDS analysis on both products revealed that the interior of the crystals still contained some Rb⁺ and Cs⁺ ions as ion exchange propagates from the edges to the core. We estimate that approximately 70% of Rb⁺ and Cs⁺ ions were exchanged with Na⁺ ions and more than 90% with Li⁺ ions based on the SEM/EDS analysis. The ionexchanged products were treated with distilled water to examine if Li⁺ or Na⁺ ions in the layers could be hydrated. No apparent changes in the interlayer spacings and crystallinity of the materials were observed.

Although the ion-exchange process is topotactic, significant changes in optical band gaps were observed. After the solid-state ion exchange with Li⁺ and Na⁺ ions the band gaps of β -CsPbBi₃Se₆ were dramatically decreased from 0.71 to 0.28 eV and 0.26 eV, respectively. This could be due to the fact that the small and hard alkali ions, Li⁺ and Na⁺, interact more strongly with the host layers via A–Se (A = Li, Na) bonding than the Rb⁺ and Cs⁺ ions. As alkali metal decreases in size, the covalent character of the A–Se bond increases and this affects the electronic band structure. Similar observations were made in the ion-exchanged products of KBi₃S₅^{33a} and K₂Hg₆S₇.^{33b}

Solution Ion-Exchange Properties of β -CsPbBi₃-Se₆ and RbPbBi₃Se₆. We subsequently explored the ability of these compounds to ion exchange in aqueous solutions of Li⁺ or Na⁺ ions and in dilute hydrochloric acid, according to the example shown in eq 2.

$$APbBi_{3}Se_{6}(s) (A = Cs, Rb) + NaI(aq) \rightarrow NaPbBi_{3}Se_{6}(s) + AI(aq) (2)$$

On treating APbBi₃Se₆ with aqueous solution of alkali iodide (1:5 by weight) or 5% HCl, rapid leaching of alkali (Cs^+, Rb^+) and Pb^{2+} ions from the compounds into the solution occurred rather than ion exchange. For example, the complete leaching of Cs⁺ ions could be achieved by treating β -CsPbBi₃Se₆ with 5% HCl (10 mL) for 5 min at room temperature. Further, a black precipitate of PbS is formed on the addition of Na₂S to the filtrate of the reaction solution, indicating that the dissolution of Pb²⁺ ion also occurred during this treatment. EDS/SEM analysis showed that the β -CsPbBi₃-Se₆ sample treated with a dilute acid solution still retained the platelike morphology of the pristine phase with the nominal composition of "PbBi₂Se₄" but X-ray powder diffraction revealed complete decomposition of the pristine phase. This leaching reaction turned out to be mainly due to the interaction of the material with water. Therefore, to minimize the leaching reaction, we tried to use a small volume of the concentrated aqueous solutions of Li⁺ and Na⁺ ions. A few drops of the solution were spread over a thin layer of the sample on a glass



Figure 9. Comparison of X-ray diffraction patterns of the products obtained from the ion-exchange reactions of β -CsPbBi₃-Se₆ with (a) 5% HCl(aq), (b) Li⁺(aq), and (c) Na⁺(aq).

slide and the reaction was monitored by X-ray diffraction as a function of time. After 20 min of reaction, we observed the shift in the interlayer spacing of (002) plane to ~ 16 Å, indicating the expansion of interlayer separation as a result of ion exchange, see Figure 9. The X-ray diffraction patterns of these products could be indexed with the hexagonal lattice parameters with a = 4.189(2) Å and c = 31.84(2) Å for Li⁺-exchanged phase $(a = 4.18(2) \text{ Å and } c = 33.08(2) \text{ Å for Na}^+$ -exchanged phase). The interlayer expansion of 3.3 Å (Li⁺-exchanged) and 3.7 Å (Na+-exchanged) accounts for a monolayer of hydrated alkali ions⁴⁸ between the host layers. SEM/EDS analysis showed the low content (<2%) of Cs⁺ ion in these products, further supporting the ion exchange of the APbBi₃Se₆ hexagonal phases under the conditions mentioned above. However, the heterogeneous distribution of the Cs⁺/Na⁺ ion contents from the edge to the core of the crystals was also observed. Furthermore, the ion-exchanged products $[A_{x}]$ $(H_2O)_y$][PbBi₃Se₆] (A = Li, Na) proved unstable and decomposed standing in air for a few days.

Concluding Remarks

A class of new quaternary compounds APbBi₃Q₆ (Q = Se, A = Cs, Rb, K; Q = S, A = Cs, Rb) with threedimensional and layered structures has been identified by the reactions of Bi and Pb in corresponding A_2Q_x fluxes. The layered compounds are only kinetically stable and they contain Bi₂Te₃-type layers, while the three-dimensional compound α -CsPbBi₃Se₆ is a thermodynamically stable phase. All compounds are n-type semiconductors with band gaps in the range of 0.27 to 0.89 eV. The existence of ternary CsBi_{3.67}Se₆, which is isostructural to α -CsPbBi₃Se₆, suggests that a variety of solid solutions with a general composition of $Cs(Pb_{1-x})$ $Bi_{0.67x}$) Bi_3Se_6 ($0 \le x \le 1$) could be formed. The layered compounds, β -CsPbBi₃Se₆ and RbPbBi₃Se₆, show ionexchange properties with Li⁺/Na⁺ ions; however the layered framework is very sensitive to long-term contact with water.

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