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Semiconducting properties and phase-matching nonlinear optical response of the one-dimensional selenophosphates ANb_2PSe_{10} (A = K, Rb, and Cs)

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ABSTRACT: The new compounds ANb_2PSe_{10} , where A = K, Rb and Cs, form from polyselenophosphate flux reactions and crystallize in the noncentrosymmetric space group *Pc*. They feature infinite one-dimensional $1/\infty[Nb_2PSe_{10}]$ chains separated by alkali cations. The chains consist of $[Nb_2(Se_2)_2]^{4+}$ clusters bridged by a diselenide and a $[PSe_4]^{3-}$ group. The chains pack differently depending on which alkali cation is present in the lattice. As a result, the analogs are not isostructural with respect to each other, and each has a different unit cell. The reaction

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chemistry involving a multitude of reaction conditions and their respective products is discussed. Other products from these reactions include NbSe₃ and Nb₂Se₉ in both crystalline and microfibrous morphologies. The ANb₂PSe₁₀ compounds are stable to oxidation in ambient air but decompose when heated above 350 °C. Their band gaps were measured to be 1.1-1.2 eV and the resistivity of the K analog at room temperature was measured at 4.5 Ω -cm. Nonlinear optical second harmonic generation measurements were done on the Rb analog yielding a $\chi^{(2)}$ of ~ 7 pm/V and showing phase matching behavior.

INTRODUCTION

Complex metal chalcophosphates display a variety of interesting physico-chemical characteristics including reversible crystal-to-glass phase transitions,^{1, 2} ferroelectricity,^{3, 4} photoluminescence,^{5, 6} super-ionic conduction,⁷ metallic conductivity⁸ and second harmonic generation (SHG).^{2, 5, 9, 10} These materials present a wide array of structural features ranging from molecular units to 3-D networks^{3, 10} reflecting the rich diversity of chalcophosphate building blocks that differ in size and shape. Examples of building blocks range from simple molecular units such as [PSe₄]³⁻, [P₂Se₆]⁴⁻ and [P₂Se₉]⁴⁻ to clusters such as [P₄Se₁₀]⁴⁻ to infinite chains like 1/x[PSe₃⁻], 1/x[P₃Se₄⁻] and 1/x[PSe₆⁻].^{3, 6, 11, 12} Despite the extensive research done on alkali metal late transition metal chalcophosphates, few reports exist on such compounds with early transition metals, especially selenium.^{5, 11, 13, 14-18} In fact, Sc, Mo, W, and Re do not have any respective chalcophosphate compounds. Some notable early transition metal quaternary chalcophosphates include NaV_{1-x}P₂S₆ and KCrP₂S₆ which are composed of [V_{1-x}P₂S₆]⁻ and [CrP₂S₆]⁻ chains respectively.^{18, 19} These compounds disperse in N-methylformamide (NMF)

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yielding gels. When dispersed in NMF, the V compound forms a vivid purple gel that exhibits liquid-crystalline behavior under the right conditions.¹⁹ Other examples are RbZrPSe₆ and CsZrPSe₆, which contains $1/\infty$ [ZrPSe₆⁻] chains and possesses a high SHG coefficient above that of AgGaSe₂, a standard of SHG and photoluminescence.⁶ K_xTaPS₆ (x ≤ 0.5) is also an interesting compound as the amount of K intercalated in the phase changes the length of the Ta-Ta bond present in the compound.¹⁵ K₃Cr₂P₃S₁₂ contains [Cr₂P₃S₁₂]³⁻ chains with Cr-Cr dimers that magnetically order below 7 K.¹⁸

Here we present three new Nb selenophosphate compounds of the family ANb_2PSe_{10} (where A = K, Rb and Cs). These materials have a noncentrosymmetric structure similar to those of the Rb and Cs containing sulfur analogs.^{16, 20} The ANb_2PSe_{10} compounds feature infinite chains that pack differently depending on which alkali metal serves as the counterion. The band gaps for each analog were measured at ~1.1 eV, and the room temperature resistivity of the K analog was measured to be 4.5 Ω -cm displaying a thermally activated temperature dependence. The compounds exhibit a significant nonlinear optical (NLO) response with phase matchable second harmonic generation (SHG).

EXPERIMENTAL SECTION

Reagents. All reagents were used as obtained from the specified supplier: potassium metal (98%, Sigma Aldrich, St. Louis, MO); rubidium metal (99.9+%, Strem Chemicals, Inc., Newburyport, MA); cesium metal (99.9+%, Strem Chemicals, Inc., Newburyport, MA); niobium metal powder (99.8% excluding Ta, Ta<1%, Alfa Aesar, Ward Hill, MA); red phosphorus powder (99%, Sigma Aldrich, St. Louis, MO); selenium pellets (99.99%, Sigma Aldrich, St Louis, MO); N,N-dimethylformamide (ACS grade, Mallinckrodt Chemical, Phillipsburg, NJ); and diethyl

ether (ACS grade, BDH Chemical, Leicestershire, U.K.). K₂Se was prepared by reaction of stoichiometric amounts of potassium and selenium in liquid ammonia as described elsewhere.²¹ Rb₂Se₂ and Cs₂Se₂ were prepared using the same procedure. P₂Se₅ was prepared by stoichiometric reaction of the elements in a 13 mm evacuated fused silica tube at 460 °C for 48 h as described elsewhere.²²

Synthesis. All compounds were synthesized by combining the respective alkali metal selenide, Nb, P_2Se_5 and Se in the appropriate ratios described below in a fused silica tube with an outer diameter of 9 mm, an inner diameter of 7 mm and a length of 20 cm inside a nitrogen filled glovebox. The tubes were flame-sealed under vacuum (~10⁻⁴ mbar), heated to 600 °C in 8 h, held there for 72 h, cooled to 350 °C in 72 h and then to room temperature in 3h. The resulting ingots were dissolved in N₂ degassed N,N-dimethylformamide (DMF) to remove the flux. Repeated washings were needed using fresh DMF every thirty min. until the solutions were no longer colored, yielding black needle-like crystals of the targeted compounds.

 KNb_2PSe_{10} (1). A mixture of 0.079 g (0.5 mmol) of K₂Se, 0.023 g (0.25 mmol) of Nb, 0.228 g (0.5 mmol) of P₂Se₅ and 0.079 g (1.0 mmol) of Se was added to a fused silica tube with an outer diameter of 9 mm, an inner diameter of 7 mm and a length of 20 cm inside a nitrogen filled glovebox. The tube was sealed under vacuum and subjected to the heating profile above. The resulting flux in the ingot was dissolved in N₂ degassed DMF yielding black, needle-like crystals of KNb₂PSe₁₀ (1). Some of the unreacted flux would not dissolve in the DMF, so percent yield could not be calculated accurately. Energy dispersive X-ray spectroscopy (EDS) analysis on several crystals gave an average stoichiometry of K_{1.0}Nb_{2.0}P_{1.1}Se_{9.6} (normalized for Nb).

 $RbNb_2PSe_{10}$ (2). A mixture of 0.164 g (0.5 mmol) of Rb₂Se₂, 0.023 g (0.25 mmol) of Nb, 0.228 g (0.5 mmol) of P₂Se₅ and 0.079 g (1.0 mmol) of Se was added to a fused silica tube with an

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outer diameter of 9 mm, an inner diameter of 7 mm and a length of 20 cm inside a nitrogen filled glovebox. The tube was sealed under vacuum and subjected to the heating profile mentioned above. The resulting flux in the ingot was dissolved in N₂ degassed DMF yielding black, needle-like crystals of RbNb₂PSe₁₀ (**2**) in 22.8 % yield. Percent yield was calculated by taking the product mass over the theoretical mass yield. EDS analysis on several crystals gave an average stoichiometry of Rb_{0.9}Nb_{2.0}P_{1.1}Se_{9.3} (normalized for Nb).

*CsNb*₂*PSe*₁₀ (3). A mixture of 0.159 g (0.375 mmol) of Cs₂Se₂, 0.023 g (0.25 mmol) of Nb, 0.228 g (0.5 mmol) of P₂Se₅ and 0.079 g (1.0 mmol) of Se was added to a fused silica tube with an outer diameter of 9 mm, an inner diameter of 7 mm and a length of 20 cm inside a nitrogen filled glovebox. The tube was sealed under vacuum and subjected to the heating profile above. The resulting flux in the ingot was dissolved in N₂ degassed DMF yielding black, needle-like crystals of CsNb₂PSe₁₀ (3) with a percent yield of 28.5 %. Percent yield was calculated by taking the product mass over the theoretical mass yield. EDS analysis on several crystals gave an average stoichiometry of Cs_{0.9}Nb_{2.0}P_{1.2}Se_{8.4} (normalized for Nb).

Single-Crystal X-Ray Crystallography. Data collections were performed on a STOE IPDS II or on a STOE IPDS 2T diffractometer using Mo K α radiation ($\lambda = 0.71073$ Å) operating at 50 kV and 40 mA at 293 K. Integration and numerical absorption corrections were performed on each structure using X-AREA, X-RED and X-SHAPE.²³ All structures were solved using direct methods and refined by full-matrix least squares on F² using the SHELXTL program package.²⁴

Powder X-Ray Diffraction. A silicon-calibrated CPS 120 INEL powder X-ray diffractometer (Cu Kα graphite-monochromatized radiation) equipped with a position-sensitive detector operating at 40 kV and 20 mA was used to collect powder X-ray diffraction (PXRD) data on

ground crystalline samples of each product with flat sample geometry. The Visualizer program within FindIt was used to generate simulated patterns using the CIF of each refined structure.

Scanning Electron Microscopy. A Hitachi S-3400 scanning electron microscope equipped with a PGT energy-dispersive X-ray analyzer was used to acquire images and semiquantitative energy dispersive X-ray spectroscopy (EDS) analyses. Spectra were collected using an accelerating voltage of 23 kV and a 30 s accumulation time. A Hitatchi S-4800 was used to get high resolution images of Nb₂Se₉ microfibers using an accelerating voltage of 2 kV.

Transmission Electron Microscopy. Samples analyzed by HRTEM were prepared by sonicating CsNb₂PSe₁₀ crystals in isopropanol for thirty min. and drop casting the dispersion onto a lacey carbon grid and which left to dry in air. The dispersed crystallites were investigated by high resolution transmission electron microscopy (Jeol-2100F HRTEM).

³¹P MAS Solid-State NMR. ³¹P magic angle spinning (MAS) NMR spectra were collected using a Varian VNMRS 400 MHz NMR. NH₄H₂PO₄ ($\delta = 0.8$ ppm) was used as a reference for chemical shifts. Pure samples of **2** were loaded into a 5 mm zirconia rotor, and experiments were performed using a pulse width (pwx90) of 3.5 µs and relaxation delay of 2 min. One scan was collected for RbNb₂PSe₁₀, with a spin rate of 5,000 rpm.

Solid State UV-Vis Spectroscopy. A Shimadzu UV-3101 PC double-beam, doublemonochromator spectrophotometer was used to collect diffuse reflectance spectra in the range of 200–2500 nm. The instrument was equipped with an integrating sphere and controlled by a personal computer. BaSO₄ was used as a standard and set to 100% reflectance. Samples were prepared by placing the ground crystalline products on a bed of BaSO₄. Collected reflectance data were converted to absorbance according to the Kubelka–Munk equation: $\alpha/S = (1 - R)2/2R$, where α is the absorption coefficient, S is the scattering coefficient, and R is the reflectance.²¹22

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Thermogravimetric Analysis. Experiments were performed using a Shimadzu TGA-50 thermal analyzer. Ground crystalline samples ($\sim 10 \text{ mg}$) were heated in Al pans in air and in nitrogen gas. The samples were heated at a rate of 10 °C/min to a maximum temperature of 600 °C.

Differential Thermal Analysis. Experiments were performed using a Shimadzu DTA-50 thermal analyzer. Ground crystalline samples ($\sim 20 \text{ mg}$) were sealed under vacuum ($\sim 10-4 \text{ mbar}$) in a fused silica ampoule. A similar amount of Al₂O₃ was sealed in a separate ampoule under vacuum and used as a reference. The samples were heated and cooled at a rate of 5 °C/min to a maximum temperature of 375 °C.

Raman Spectroscopy. Raman spectra were collected of ground crystalline samples on a DeltaNu Advantage NIR spectrometer equipped with a CCD detector. The beam source was emitted from a diode laser with 785 nm radiation. The samples were loaded into borosilicate glass capillaries for the measurement. A max power of 60 mW and beam diameter of 35 μ m were used. The spectrum was collected using an integration time of 10 s.

Electrical conductivity. Standard four probe measurements were performed to determine the temperature dependent resistivity of **1**. Sliver epoxy H20E was applied to make contacts on a small single crystal. Contact resistance can be significantly reduced after annealing at 220 °C for 1h in a protection of Argon gas. After annealing, samples were immediately transferred to the Physical Properties Measurement System (PPMS, Quantum Design) at Argonne National Lab. A current of 10 nA was applied along the longest axis of the crystal.

Magnetic susceptibility. Magnetic susceptibility measurements were performed using a Quantum Design MPMS-XL in the temperature range of 1.8 K to 300 K at a field of 1 T. Ground samples of **2** were prepared by placement in a polycarbonate capsule then restrained with eicosane.

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Nonlinear Optical (NLO) Measurements. Crystalline powders of **2** were analyzed for second harmonic generation (SHG) measurements after sieving in the size ranges of $20 - 32 \mu m$, $32 - 45 \mu m$, $45 - 53 \mu m$, $53 - 63 \mu m$, $63 - 90 \mu m$, $90 - 106 \mu m$, $106 - 125 \mu m$, and $125 - 150 \mu m$ to examine the phase-matching behavior of the sample. The sieved particles were enclosed in quartz capillary tubes, which were flame sealed to prevent exposure to air and moisture during the measurement. Each tube was loaded into a homemade sample holder mounted on a Z-scan translation stage. The SHG efficiencies of the samples were directly compared with that of a reference nonlinear optical (NLO) material, AgGaSe₂, prepared in a similar fashion.

Broadband SHG experiments were conducted at room temperature. In order to generate tunable pulses, coherent light of 1064 nm wavelength was first produced using an EKSPLA PL-2250 series diode-pumped picosecond Nd:YAG laser with a pulse width of 30 ps and a repetition rate of 50 Hz. The Nd:YAG laser pumped an EKSPLA Harmonics Unit (HU) H400 where the input beam was frequency tripled by a successive cascade of NLO wave mixing. The 1064 nm and frequency-tripled radiation (355 nm) from the HU entered an EKSPLA PG403-SH-DFG Optical Parametric Oscillator (OPO) composed of four main parts; a double-pass parametric generator, a single-pass parametric amplifier, a second harmonic generator, and a difference frequency generation scheme. The output wavelengths of the OPO used in the experiments ranged from 2300 nm to 4100 nm at increments of 200 nm; since the bandgap of the compound is about 1.1 eV (~ 1130 nm), typical SHG scans in the range of 1100 – 2100 nm were not performed in order to avoid possible sample damage by 2-photon excitation. The corresponding SHG wavelength range is therefore $\lambda_{SHG} = \lambda/2 = 1150 - 2050$ nm.

The incident pulse energy was tuned to 20 μ J before being mildly focused onto samples with a spot size of ~0.5 mm in diameter by a CaF₂ convex lens far away from the focus. Here the beam

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spot size was deliberately determined in order to i) properly average the SHG signal from powders of random orientations and ii) to minimize the change in the spot size when we swept the fundamental wavelength λ over a broad range (2300 – 4100 nm); the beam waist w_0 at the Zscan focus undergoes a significant λ -dependent variation via $w_0 = (\lambda / \pi)(f/\sigma)$, where f and σ are the focal length and the Gaussian width of the incident beam, respectively.²⁵ The NLO signals from the samples were collected using a reflection geometry and a fiber-optic bundle, which was coupled to a selective-grating (300 grooves/mm) spectrometer equipped with an extended InGaAs (Symphony) detector. We confirmed that any surface-induced effects, as well as SHG signals from other optical components were negligible. The relative SHG signals spectrally resolved in a broad wavelength range were precisely calibrated with the known and measured efficiencies of all optical components. No sample damage was induced by the laser pulses within the experimental conditions.

RESULTS AND DISCUSSION

Synthesis and reaction chemistry. Synthesizing pure phases of ANb₂PSe₁₀ is a challenge, and little is understood of what mechanisms are dominant in selenophosphate fluxes. We therefore find it important to document reaction conditions and the resulting products to better understand how flux composition and reaction temperature affect product formation when Nb is present. The ANb₂PSe₁₀ compounds were first observed in reaction carried out at 800 °C in an A/P/Se flux. At this temperature, the major products are actually NbSe₂ and Nb₂Se₉ with ANb₂PSe₁₀ forming as a minor phase. In order to increase the fraction of ANb₂PSe₁₀ in the product, lower temperatures were used (700-600 °C). Though lower temperatures did improve the ANb₂PSe₁₀ to binary phase ratio, the flux composition also had to be altered to further increase purity. Originally, the A₂Se_x :

Nb : P_2Se_5 : Se reactant ratio began at 2:1:2:7 (x = 1 when A = K, x = 2 when A = Rb or Cs). Flux basicity was elevated by decreasing the relative fraction of elemental Se which proved to significantly suppress the amount of Nb₂Se₉/NbSe₂ in the product. It was also found that shorter soak times produced less of the thermodynamically stable binaries, while longer soak times favored Nb₂Se₉/NbSe₂ formation. The optimum conditions for obtaining the highest purity were at 600 °C using a A_2Se_x : Nb : P_2Se_5 : Se ratio of 2:1:2:4 for KNb₂PSe₁₀ (1) and RbNb₂PSe₁₀ (2) and using a $C_{s_2}Se_2$: Nb : P₂Se₅ : Se ratio of 3:2:4:8 for $C_sNb_2PSe_{10}$ (3). Good agreement was obtained between the calculated and experimental powder X-ray diffraction patterns of 2 and 3 (See Figure 1). ³¹P MAS solid state NMR spectroscopy also supports the isolation of **2** with no secondary P-containing phases present (see supporting information). Despite multiple attempts to remove the other phases, compound 1 always formed with some unknown secondary phase as suggested by extra weak Bragg peaks present in the powder x-ray diffraction (PXRD) patterns (Figure 1). These insoluble phases most likely come from flux constituents. Sodium analogs of the title compounds were also targeted, but no quaternary phases were observed, Nb₂Se₉ being the only product of these reactions.

The effect of tuning the basicity of the flux (or electron donating ability of the flux)¹ by using different equivalents of K_2Se in the flux, were also investigated. It is interesting that lowering the relative ratio of K_2Se : Nb down to 1:1, i.e. decreasing flux basicity, led to the formation of Nb₂Se₉ microfibers at 800 °C along with 1. Most of the microfibers had a diameter of around 500 nm with a size distribution from 50 nm to 1 μ m (Figure 2). NbSe₃ has been reported crystallizing in a microfibrous form,²⁶ however, Nb₂Se₉ has not been reported with such a morphology.²⁶⁻²⁹ Although it is unclear how the microfibers grow, the presence of K₂Se and/or P₂Se₅ in the reaction seems to promote their growth. As Nb₂Se₉ is also one-dimensional in

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nature,²⁷ it is possible that the K^+ ions in the flux help impedes crystal growth perpendicular to the fiber direction, promoting formation into microfibers instead of thick rods. It is also intriguing to consider that Nb₂Se₉ could be an intermediate phase in the formation of KNb₂PSe₁₀, or vise versa, as their chain structure is similar.

At lower temperatures, increasing the relative amount of A_2Se_x in the A_2Se_x : Nb : P_2Se_5 : Se mixture to 3:1:2:4 (i.e. increasing flux basicity) made the resulting flux difficult to dissolve in DMF, resulting in left over flux in the ANb₂PSe₁₀ product. When four equivalents of K₂Se were used (4:1:2:4 ratio) with a soak temperature of 600 °C, K₄P₂Se₆ began forming as a product while at five equivalents the reaction gave Nb₂Se₉ and K₄P₂Se₆ with no 1 present, suggesting that a flux that is too basic destroys the chains of 1. Lowering the amount of K₂Se below two equivalents in its respective reactions resulted only in Nb₂Se₉. In the case of the Cs analog, lowering the amount of Cs₂Se₂ down to 1.5 equivalents yielded pure CsNb₂PSe₁₀ with no secondary phases.

Direct combination reactions (using a 1:4:1:14 ratio of K_2Se : Nb : P_2Se_5 : Se) at 700 °C did not yield crystals of **1**. Instead, only NbSe₃ microfibers were found, though minor peaks of **1** could be observed in the product's PXRD pattern. At 600 °C with a ratio of 2:1:2:4 of Rb₂Se₂ : Nb : P_2Se_5 : Se, **2** was observed in pure form with no secondary phases present while compound **3** formed as a single phase with a ratio of 3:2:4:8 of Cs_2Se_2 : Nb : P_2Se_5 : Se. EDS analysis on multiple crystals of each compound yielded consistent compositions close to those obtained from single-crystal refinement (see experimental section). See Table 3 for a summary of reaction conditions and the resulting products. Although there are several niobium based thiophosphates such as $ANb_2P_2S_{12}$ and $Cs_{0.49}NbPS_6$, in this work we did not observe any corresponding selenophosphate phases as analogs of these systems.^{17, 30}

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Of the three analogs, **2** crystallizes easiest as the reactant ratios can vary slightly while still yielding a pure, isolated phase. Compound **2** tends to grow larger crystals than those of other analogs, and the flux of such reactions dissolves quickly in DMF. Conversely, **1** and **3** do not crystallize easily and form as a single phase using only very specific equivalents of reactants. Compound **3** formed as a pure phase only at the reactant ratio listed above, and altering it in any way yielded either secondary phases or a Cs/P/Se flux that would not dissolve easily in DMF. Despite multiple attempts, compound **1** could not be formed as a single phase due to the insolubility of the K/P/Se flux or formation of secondary phases.

Solubility and dispersion. All ANb_2PSe_{10} compounds are stable to oxidation or hydrolysis by air or water in ambient conditions. They are insoluble in DMF, N-methylformamide (NMF), ethanol, methanol, formamide and acetonitrile and do not decompose in these solvents, while the compounds decompose in hydrazine. All analogs disperse well in isopropanol, water and acetonitrile after 30 min of sonication forming a black, cloudy liquid in both air and N₂ atmosphere. Dispersions prepared in air using isopropanol and acetonitrile oxidized after a day, while dispersions in inert atmosphere lasted over a week, though there was some settling. Compounds dispersed in water decomposed over the course of several hours changing the color of the dispersion from black to brown (presumably hydrolysis) whether in air or N₂ atmosphere.

Dispersions in H₂O, isopropanol and acetonitrile were immediately drop cast onto glass plates, heat dried and analyzed by PXRD. The resulting patterns showed that the deposited solids were crystalline, possessing the same 1-D structure (Figure 3). This is further supported by TEM experiments of the drop cast dispersion on a lacey carbon grid where micro- and nano-sized crystallites were observed (see supporting information). This suggests that the ANb₂PSe₁₀ systems may be processable into films using such dispersions.

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Crystal Structure Description. Compounds 1, 2 and 3 crystallize in the polar monoclinic space group Pc (No. 7), which is in the polar point group m of the 2/m Laue class. The structure contains infinite chains $[Nb_2PSe_{10}]^-$ similar to $[Nb_2PS_{10}]^{1-}$ chains from compounds of the family ANb_2PS_{10} (A = Na, Ag, K, Rb or Cs).^{14, 16, 20, 31} The chains consist of $[Nb_2(Se_2)_2]^{4+}$ clusters bridged by a $[Se_2]^{2-}$ and a $[PSe_4]^{3-}$ unit (Figures 4, 5, 6). There are a total of three different diselenide groups in the structure, each with a -2 charge. Combined with the $[PSe_4]^{3-}$ unit, this gives a total anionic charge of -9 to the selenide and selenophosphate groups. The single alkali cation leaves a charge of -8 to be countered by two Nb atoms, giving them both an oxidation state of +4. The $[Nb_2(Se_2)_2]^{4+}$ clusters contain a Nb-Nb bond (2.960(2)-2.968(1) Å). The metalmetal bond formed by the d¹-d¹ interaction between the Nb⁴⁺ centers makes the compound diamagnetic, which is supported via magnetic susceptibility measurements (See section below).

The Nb⁴⁺ centers coordinate to eight Se atoms in a distorted, bi-capped trigonal prism (Figure 6b). Each bi-capped trigonal prism is face-sharing on one side and edge-sharing on the other. Compound **2** is isostructural to its sulfur containing counterpart $RbNb_2PS_{10}$.¹⁶ However, neither **1** nor **3** are isotypic with the sulfur analogs.

All Nb-Se bonds are normal and fall within 2.598(2) to 2.777(2) Å, (Table 2). They can be categorized in 4 types (from shortest to longest): those to the Se atoms in the $[Nb_2(Se_2)_2]^{4+}$ cluster (2.593(2) - 2.675(2) Å), those to the diselenides bridging the clusters (2.681(2) - 2.731(1) Å), those to the Se atoms that are monodentate to the Nb⁴⁺ in the $[PSe_4]^{3-}$ unit (2.710(2) - 2.774(2) Å) and those to the bridging Se in the $[PSe_4]^{3-}$ unit (2.769(1) - 2.784(1) Å). The bonds in the $[Nb_2(Se_2)_2]^{4+}$ cluster are shorter due to the presence of the Nb-Nb bond, which not only brings the metals closer to each other, but closer to the Se atoms as well. The Nb-Se bonds with the $[PSe_4]^{3-}$ unit are the longest most likely due to the highly covalent nature of the P-Se bonds

which are much shorter (2.200(4) - 2.232(4) Å). This leaves less electron density available for the Nb-Se bond, making them weaker than other Nb-Se bonds in the structure.

There are three types of P-Se bonds present in the structures associated with triply bridging, doubly bridging and terminal Se atoms. All P-Se bonds are within the normal range (Table 2). Being terminal atoms, Se10 and Se20 have shorter bond distances and greater thermal displacement parameters $(20(1)-36(1) \text{ Å}^2 \times 10^3)$. The [PSe₄]³⁻ tetrahedron has angles ranging from 112.0° to 115.7° to the terminal Se, and 99.2° - 103.0° from the triply bridging Se to the doubly bridging Se atoms. This arises because the Nb centers cause the bonded Se atoms to close in towards each other, widening the angles to the terminal Se.

Despite adopting the same space group and chain structure, the unit cells vary with alkali metal cation. As the size of the cation increases, the packing of the chains changes which alters the unit cells. Comparing the K and Rb analog, the difference in the chain packing can be seen in the *b* axis projections of each system (Figures 5, 7). The unit cell dimension *b* is halved due to better chain alignment in the [010] direction from **1** to **2**. As a result, **1** has two crystallographically unique chains that are chemically identical while **2** has only one crystallographically unique chain. The reasons for this are unclear, but it is possible that the Rb⁺ ions are the appropriate size to fit in between the chains in "pockets" present in the asymmetric gap bridging the $[Nb_2(Se_2)_2]^{4+}$ clusters. K⁺ ions are a bit too small to fit in these pockets, and so the chains must shift to compensate (see supporting information for Rb⁺ ion coordination). From **2** to **3**, the chains shift in relation to each other along the chain direction ([001] direction) causing the unit cell dimension *a* to double and yielding two chemically identical, yet crystallographically unique chains (Figures 5, 8). Cs⁺ ions are larger than Rb⁺ ions, and therefore cannot fit in the pockets with the chains remaining in their original positions. As a result, the chains must shift to create

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room for Cs^+ to fit in the pocket. This "chain slide" along the *c* axis prevents the chains from aligning in the [100] direction as they do in **1** and **2**. This also reduces the β angle of the unit cell of **3**. The unit cell dimension *c* stays fairly constant in all analogs as it is primarily representative of the periodicity within in the chains themselves.³³

The interchain distance in **1**, **2** and **3** along the *a* axis increases from 7.131(3) to 7.218(2) to 7.324(2) Å, respectively, consistent with the increasing size of the alkali atoms. However, along the *b* axis, the nearest neighbor Se⁻⁻Se distance (which is van der Waals in character) increases from 3.328(2) Å in **1** to 3.423(2) Å in **2**, and then decreases to 3.379(2) Å in **3**. This is unusual behavior since the larger Cs⁺ ions should create more space in between the chains by pushing them farther apart. This surprising decrease in the Se⁻⁻Se interchain distance from the Rb to the Cs analog can be explained by the chain shift along the *c* axis. Because Cs⁺ ions cannot fit into the smaller interchain pockets formed in **2**, the chains are forced to slide to a different position entirely with respect to their neighbors in order to make a bigger pocket for Cs⁺ ion. This is visually obvious with respect to the *a* axis, but the shift also affects how the chain interaction along the *b* axis, bringing the chains closer together in that direction. In this way, the position and size of the Cs⁺ cations in compound **3** separate the chains along the *a* axis, but brings the chains closer together along the *b* axis, but brings the chains along the *b* axis.

The fact that **2** forms much easier than **1** or **3** could likely be due to the size of the cations and how well they fit into the available pockets between the chains. Rb^+ ions fit well into the pockets between the chains, and since the chain structure stays constant between analogs, the pocket size between chains want to stay constant. As a result, when the cation size changes, the resulting configuration is energetically less favorable. For example, in compound **1** the K⁺ ions are smaller, forcing every other chain to offset slightly so that the K⁺ ions can still fit into the

pockets. This creates an energetically unfavorable configuration since the chains are forced closer together. This hampers the growth of the crystals, causing their formation to be slower than that of **2**. The same can be said for **3** except with the larger Cs^+ ions causing the chains to shift.

Thermal Properties. Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) were performed on all analogs of ANb_2PSe_{10} (Figure 9). The samples experience a great mass loss in air and in nitrogen atmospheres above 375 °C. No distinct thermal events, however, were observed up to this temperature via DTA. PXRD patterns of the DTA products of 1 and 2 support the lack of formation of a second phase, showing no change in the patterns before and after analysis. However, the DTA product of 3 contains Nb₂Se₉ as judged by the PXRD pattern (See supporting information). The absence of any detectable thermal DTA events suggests that Nb₂Se₉ formed gradually in 3 as the system was heated up to 375 °C.

³¹P MAS Solid-State NMR. NMR spectra taken from a polycrystalline sample of **2** show one peak at -8.32 ppm, confirming that all phosphorus atoms in the structure are in the same chemical environment. The spectra also confirm that **2** was obtained pure with no phosphorus containing second phases present. Compared to other known selenophosphate groups in ³¹P MAS solid state NMR, **2** shows a shift that is more negative by 38.32 and 19.21 ppm, respectively, than those of the one-dimensional RbZrPSe₆ and of the [PSe₄]³⁻ group in the molecular species [W(PSe₄)(PSe₂)(Se)]^{2-,6, 34} This demonstrates that the phosphorus in **2** is more shielded than in the other two compounds directly resulting from [PSe₄]³⁻ group being bound to a less electropositive Nb⁴⁺ center as compared to Zr⁴⁺ or W⁴⁺. Cu₃PSe₄ and KPbPSe₄, referenced using H₃PO₄ ($\delta = 0$ ppm), have a shift of -83.3 and -74.3 ppm respectively, which is quite a bit more negative than the shift of -8.32 ppm in **2**.³⁵ However, this great difference is due to the fact that

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both of these compounds are 3D networks and also due to the different oxidation states of the metals present in these two compounds. The $[PSe_4]^{3-}$ unit in these compounds have every Se bonded to the metal, creating a dissimilar environment for the unit. This combined with the fact that the metal ions have a much lower oxidation state than that of Nb⁴⁺ gives Cu₃PSe₄ and KPbPSe₄ a significantly more negative ³¹P NMR shift.

Optical Absorption Spectroscopy. Optical diffuse reflectance spectra converted to absorbance indicate an energy band gap in the range of 1.1-1.2 eV for all three compounds. The band gap transition is expected to be primarily from the Se orbitals in the valence band to the Nb orbitals in the conduction band due to excitations occurring in the $[Nb_2PSe_{10}]^-$ chains. This hypothesis is based on band valence calculations from other selenophosphate materials.^{12b, 37} There is a slight decrease in band gap as the alkali cation size increased, most notably from **2** to **3** (Figure 10). This small change could be the result of the shortening nearest neighbor distance from **2** to **3**, but this explanation does not account for the even shorter Se^{...}Se distances present in **1**, which has a slightly larger band gap. All compounds decomposed under laser illumination at 785 nm, the Raman laser wavelength, so no relevant Raman spectra could be collected.

Electrical Properties. The electrical resistivity of a single crystal of 1 was measured versus temperature (Figure 11). The resistivity of the crystal at 293 K was measured at ~4.5(2) Ω -cm. The data shows semiconductor behavior since the resistance increases as temperature decreases. This is consistent with the material's relatively low band gap of 1.1 eV. The activation energy was calculated using the relationship:

$$\rho \propto \exp(E_a/2kBT)$$
 1

which can be simplified to $E_a = c*2*kB$ by plotting $ln(\rho)$ vs 1/T to find the activation energy, Ea, where kB is the Boltzmann constant in eV/K, and c is the slope of the line plotted.³⁸ The

activation energy was calculated to be 0.25(1) eV (Figure 11(inset)). This activation energy corresponds to an energy gap of $2E_a \sim 0.5$ eV which is smaller than the optically measured band gap. This suggests that the conductivity does not lie within the intrinsic regime of the compound due to the divergence between the measured optical and electrical bandgaps. Therefore the energy gap of ~0.5 eV is likely associated with extrinsic deep defects in the structure.

Magnetic Susceptibility. Compound **2** was measured for the molar magnetic susceptibility (χ_m) as a function of temperature at 1 Tesla (see supporting info). The compound is diamagnetic for the entire temperature range (300 to 1.8 K). This is consistent with the fact that the Nb⁴⁺ centers have no unpaired electrons due to strong spin-spin coupling in the Nb-Nb bond. A Curie tail is seen at low temperatures indicating the presence of a paramagnetic impurity. Fitting the Curie tail to the function $1/\chi_m$ and assuming a spin of $\frac{1}{2}$ for the impurity gives a molar percent of paramagnetic impurity of 0.3 %. This low percentage of impurity is not detectable by PXRD.

Nonlinear Optical Properties and Second Harmonic Generation. The wavelengthdependent SHG response of **2** and the AgGaSe₂ reference (Figure 12) was obtained using a particle size of $106 - 125 \,\mu\text{m}$. Significantly reduced SHG counts of the $\lambda/2$ beam at $\lambda_{\text{SHG}} = 1150$ nm are common for both sample and reference of all particle sizes. This effect arises from linear absorption of the fundamental beam by the capillary tube.³⁹ This, however, does not affect the estimation of the SHG coefficient of the sample as explained below. The observed wavelengthdependent SHG from AgGaSe₂ is reasonably consistent with previous results.⁴⁰ Interestingly, samples of **2** yielded a relatively "flat" SHG dispersion over the experimental wavelength range. It was also confirmed that multiphoton absorption of the fundamental beam by the sample was negligible for the input laser intensity used.

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The most important factor in the selection of a potential NLO material for wavelength conversion is phase-matchability. In order to investigate the phase-matching behavior, SHG particle-size dependence of **2** and AgGaSe₂ were conducted at $\lambda = 3300$ nm (Figure 13). An increasing trend with particle size in Figure 13a clearly indicates that compound **2** is type-I phase-matchable with the fundamental beam at $\lambda = 3300$ nm. AgGaSe₂ becomes phase-matchable for $\lambda > 3000$ nm,⁴¹ which is also supported by the relatively flat trend of the particle size dependence in Figure 13b. Therefore, the SHG coefficient of **2** was estimated by directly comparing the reference material in the phase-matching regime as detailed below.

AgGaSe₂ is the benchmark mid-IR NLO material with a static SHG coefficient of $\chi^{(2)} = 66$ pm/V ($\lambda \rightarrow \infty$).⁴² By using AgGaSe₂ as a reference material with a known $\chi^{(2)}$ value, the $\chi^{(2)}$ of **2** was measured by comparing the SHG response at the static range in which both the reference and sample are phase-matchable with minimal absorption effects. Using the Kurtz powder method,⁴³ the static value of $\chi^{(2)}$ of **2** can be calculated by comparison with the reference;

$$\chi_{\mathcal{S}}^{(2)} = \chi_{\mathcal{R}}^{(2)} \left(\frac{l_{\mathcal{S}}}{l_{\mathcal{R}}}\right)^{1/2} \qquad 2$$

where I_S and I_R are the experimentally measured SHG counts from the sample and reference, respectively (Figure 14). The calculation yields that $\chi^{(2)}(\text{RbNb}_2\text{PSe}_{10}) \sim 7 \text{ pm/V}$.

CONCLUSIONS

New semiconducting compounds KNb_2PSe_{10} , $RbNb_2PSe_{10}$ and $CsNb_2PSe_{10}$ consisting of $1/\infty$ [Nb₂PSe₁₀⁻] chains form from reactions in polyselenophosphate fluxes. The orientation of the chains with respect to the unit cells differs between the alkali salts, but the overall chemical structure is otherwise similar and noncentrosymmetric in nature. The compounds possess band

gaps of ~1.1-1.2 eV and decompose when heated above 350 °C. SHG analysis of the Rb analog states that it is phase-matchable with a $\chi^{(2)}$ of ~ 7 pm/V. The ANb₂PSe₁₀ system shows the subtle but interesting effect that alkali metal counterion size can have on chain packing. While many materials simply expand their lattice parameters or change their crystallization completely,⁴⁴ this system changes its chain packing instead.

Finally, it is interesting that more elemental selenium and less alkali selenide in the reaction mixture defines a new method for the production of Nb₂Se₉ and NbSe₂. Reducing the alkali selenide further while adding more elemental selenium favors formation of NbSe₃ and Nb₂Se₉. When the relative fractions of Nb and Se increase in the reaction mixture at higher temperatures, the morphology of NbSe₂ and Nb₂Se₉ changes to microfibers. This implies that this type of reaction may also be used as a convenient procedure to produce high yield samples of these binary materials in microfibrous form.

ASSOCIATED CONTENT

Supporting Information.

³¹P MAS Solid State NMR, the coordination environment of Rb⁺ in RbNb₂PSe₁₀, TEM of CsNb₂PSe₁₀ crystallites from an isopropanol dispersion, magnetic susceptibility data, PXRD of DTA products and crystallographic information files (CIF) can be found in the supporting information. This material is available free of charge via the internet at http://pubs.acs.org.

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Author Contributions

The manuscript was written through contributions of all authors. SHG section and data by Daniel J. Clark, Felix O. Saouma and Professor Joon I. Jang. Magnetic susceptibility data by Samantha M. Clarke and Professor Danna Freedman. Resistivity data by Lei Fang. All authors have given approval to the final version of the manuscript.

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Notes

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ABBREVIATIONS

DMF, N,N-dimethylformamide; DTA, Differential Thermal Analysis; EDS, Energy Dispersive x-ray Spectroscopy; HU, Harmonics Unit; NLO, Nonlinear Optical; NMF, N-methylformamide; OPO, Optical Parametric Oscillator; SEM, Scanning Electron Microscopy; SHG, Second Harmonic Generation; PXRD, Powder X-Ray Diffraction; TEM, Transmission Electron Microscopy; TGA, Thermogravimetric Analysis

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Compound	I	2	3	
Empirical Formula	KNb ₂ PSe ₁₀	RbNb ₂ PSe ₁₀	CsNb ₂ PSe ₁₀	
Formula weight	1045.49	1091.86	1139.30	
Wavelength, Å	0.71073	0.71073	0.71073	
Habit	needle	needle	needle	
Color	black	black	black	
Crystal system	monoclinic	monoclinic	monoclinic	
Space group	Рс	Pc	Pc	
<i>a</i> , Å	7.2931(6)	7.3810(15)	14.626(3)	
b, Å	15.612(2)	7.836(2)	7.810(2)	
<i>c</i> , Å	13.557(3)	13.564(3)	13.553(3)	
β, (deg)	106.64(3)	106.75(3)	98.56(3)	
<i>V</i> , Å ³	1479.0(2)	751.2(3)	1530.9(5)	
Z	4	2	4	
ρ , g/cm ³	4.695	4.827	4.943	
μ , mm ⁻¹	26.509	29.039	27.684	
F(000)	1824	948	1968	
θ_{max} , deg	34.89	34.84	36.43	
Reflections collected	22086	12251	24816	
R _{int}	0.0710	0.0563	0.0550	
No. parameters	253	128	254	
Refinement method	Full matrix least-squares on F ²			
GooF	1.063	1.055	1.085	
Final R indices [> $2\sigma(I)$], R1/wR2	0.0571/0.1308	0.0461/0.1067	0.0577/0.1108	
R indices (all data), R1/wR2	0.0728/0.1387	0.0600/0.1239	0.0820/0.1214	

Table 2. Selected b	ond lengths (Å) for AN	$b_2 PSe_{10}$ (A = K, Rb, and	Cs)	
Atoms	KNb ₂ PSe ₁₀	RbNb ₂ PSe ₁₀	CsNb ₂ PSe ₁₀	
Nb(1)-Nb(2)	2.9589(14)	2.9675(11)	2.9626(11)	
Nb(3)-Nb(4)	2.9661(14)		2.9647(12)	
Nb(1)-Se(1)	2.762(2)	2.7738(15)	2.7244(15)	
Nb(3)-Se(11)	2.766(2)		2.7102(15)	
Nb(1)-Se(2)	2.776(2)	2.7823(15)	2.7770(14)	
Nb(3)-Se(12)	2.770(2)		2.7687(14)	
Nb(2)-Se(2)	2.770(2)	2.7737(14)	2.7841(12)	
Nb(4)-Se(12)	2.776(2)		2.7816(13)	
Nb(1)-Se(3)	2.717(2)	2.7300(14)	2.6829(13)	
Nb(3)-Se(13)	2.732(2)		2.6807(14)	
Nb(2)-Se(3)	2.688(2)	2.6814(15)	2.7349(14)	
Nb(4)-Se(13)	2.676(2)		2.7311(14)	
Nb(1)-Se(4)	2.710(2)	2.7076(13)	2.6914(13)	
Nb(3)-Se(14)	2.707(2)		2.6990(13)	
Nb(2)-Se(4)	2.707(15)	2.7040(13)	2.6969(13)	
Nb(4)-Se(14)	2.702(2)		2.7011(13)	
Nb(2)-Se(5)	2.712(2)	2.7158(15)	2.7471(15)	
Nb(4)-Se(15)	2.714(2)		2.7709(15)	
Nb(1)-Se(6)	2.656(2)	2.6563(15)	2.6624(15)	
Nb(3)-Se(16)	2.645(2)		2.655(2)	
Nb(2)-Se(6)	2.613(2)	2.6042(14)	2.6061(14)	
Nb(4)-Se(16)	2.598(2)		2.6098(15)	
Nb(1)-Se(7)	2.602(2)	2.616(2)	2.5957(15)	
Nb(3)-Se(17)	2.621(2)		2.5976(15)	
Nb(2)-Se(7)	2.642(2)	2.6541(14)	2.6648(15)	
Nb(4)-Se(17)	2.649(2)		2.6572(15)	
Nb(1)-Se(8)	2.618(2)	2.6062(13)	2.5963(14)	

Nb(3)-Se(18)	2.600(2)		2.5927(15)	
Nb(2)-Se(8)	2.675(2)	2.6745(16)	2.6840(15)	
Nb(4)-Se(18)	2.666(2)		2.660(2)	
Nb(1)-Se(9)	2.647(2)	2.6731(14)	2.6635(14)	
Nb(3)-Se(19)	2.679(2)		2.6691(14)	
Nb(2)-Se(9)	2.604(2)	2.6053(14)	2.5925(15)	
Nb(4)-Se(19)	2.608(2)		2.6063(15)	
Se(3)-Se(4)	2.328(2)	2.3318(14)	2.330(2)	
Se(13)-Se(14)	2.333(2)		2.329(2)	
Se(6)-Se(7)	2.293(2)	2.294(2)	2.297(2)	
Se(16)-Se(17)	2.293(2)		2.289(2)	
Se(8)-Se(9)	2.312(2)	2.315(2)	2.312(2)	
Se(18)-Se(19)	2.313(2)		2.309(2)	
Se(1)-P(1)	2.210(3)	2.220(3)	2.200(3)	
Se(11)-P(2)	2.221(3)		2.213(3)	
Se(2)-P(1)	2.232(4)	2.236(3)	2.232(3)	
Se(12)-P(2)	2.230(4)		2.231(3)	
Se(5)-P(1)	2.212(3)	2.202(3)	2.206(3)	
Se(15)-P(2)	2.200(4)		2.212(3)	
Se(10)-P(1)	2.135(4)	2.137(3)	2.138(3)	
Se(20)-P(2)	2.138(4)		2.133(3)	

Table 3. SummaryMajor products are	of react shown in	ion co bold.	onditions	and the	ir respective products ($A = K$, Rb and Cs).
	Stoichiometric equivalents of			ents of	
Temperature (°C)	A ₂ Se _x	Nb	P ₂ Se ₅	Se	Reaction Product
800	2	1	2	7,6	Nb_2Se_9 , $NbSe_2$
800	2	1	2	5-2	Nb_2Se_9 , $NbSe_2$, ANb_2PSe_{10}
800	1	1	2	5	Nb₂Se₉ (microfibers) , ANb ₂ PSe ₁₀
700	2	1	2	5-3	ANb ₂ PSe ₁₀ , NbSe ₂
700	1	4	1	7	NbSe₃ (microfibers) , ANb ₂ PSe ₁₀
600	3	1	2	4	Unreacted flux, ANb ₂ PSe ₁₀
600	4	1	2	4	Unreacted flux, ANb ₂ PSe ₁₀ , K ₄ P ₂ Se ₆
600	5	1	2	4	Unreacted flux, Nb ₂ Se ₉ , K ₄ P ₂ Se ₆
600	2, 1.5	1	2	4,3	ANb ₂ PSe ₁₀



Figure 1. Experimental powder X-ray diffraction patterns of ANb_2PSe_{10} (A = K, Rb and Cs) compared to calculated patterns.



Figure 2. SEM images of Nb₂Se₉ microfibers at a a) lower resolution, and at b) a higher resolution. Microfibers range from 50 nm to 1 μ m in width. The white dots present are flecks of selenium leftover from flux dissolution. Fleck formation can be easily prevented if the flux dissolution in DMF is kept oxygen free and the DMF is replaced every 30 min .



Figure 3. PXRD patterns of $RbNb_2PSe_{10}$ freshly dispersed in H₂O, isopropanol, and acetonitrile which were drop cast onto glass plates. The pattern shows that the samples still retain some crystallinity.





Figure 5. a) RbNb₂PSe₁₀ along the [100] direction. b) RbNb₂PSe₁₀ along the [010] direction.



Figure 6. a) $RbNb_2PSe_{10}$ along the [001] direction. b) A polyhedra view of the Nb center coordination environment. The bicapped trigonal prisms are outlined in black and are face-sharing on one side and edge sharing on the other.



Figure 7. a) $\text{KNb}_2\text{PSe}_{10}$ along the [010] direction. Notice that chains along the [010] direction do not perfectly overlap causing *b* to double. b) $\text{KNb}_2\text{PSe}_{10}$ along the [100] direction. The unit cell dimension *b* is doubled compared to the Rb and Cs analog.



Figure 8. a) $CsNb_2PSe_{10}$ along the [010] direction. The unit cell dimension *a* is doubled compared to the K and Rb versions. The arrow depicts the chain slide of every other chain of the structure. b) $CsNb_2PSe_{10}$ along the [100] direction. Unlike K and Rb versions, it is impossible to align the chains perfectly in the crystal along the *ac* plane.



Figure 9. a) TGA of ANb_2PSe_{10} (A = K, Rb, or Cs). All compounds oxidize slightly then decompose above 375 °C in air. Percent mass loss was calculated as (current mass)/(initial mass). b) DTA data of ANb_2PSe_{10} . No peaks were detected in all samples.



Figure 10. Optical absorption spectra of ANb_2PSe_{10} (A = K, Rb, or Cs). The K analog band gap was measured to be around 1.19 eV, the Rb to be 1.15 eV, and the Cs band gap to be 1.07 eV.



Figure 11. Resistivity vs temperature of a single crystal sample of KNb_2PSe_{10} . As the temperature decreases, the resistivity increases indicating semiconductor behavior. The room temperature resistivity was measured at 4.5 Ω -cm. Inset: the natural log of resistivity vs inverse temperature. The activation energy was obtained by fitting the linear portion.



Figure 12. SHG response as a function of wavelength from powder samples of (a) RbNb₂PSe₁₀ and (b) AgGaSe₂ in the range of $\lambda_{inc} = 2.3 - 4.1 \ \mu m$.



Figure 13. Particle-size dependence of SHG in (a) RbNb₂PSe₁₀ and (b) AgGaSe₂ at $\lambda = 3.3 \mu m$.



Figure 14. SHG response comparison of RbNb₂PSe₁₀ with AgGaSe₂. SHG counts were compared at the long-wavelength limit (1650 nm) where RbNb₂PSe₁₀ could be compared with AgGaSe₂ fairly. The dotted lines signify where the SHG counts were compared for both compounds to obtain $\chi^{(2)}$ of RbNb₂PSe₁₀.

TOC Graphic

