# Room Temperature Light Emission from the Low-Dimensional Semiconductors AZrPS$_6$ (A = K, Rb, Cs)

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Solid state light emitting semiconductor materials are of significant technological interest as they impact numerous applications including solid state lighting technology, medical and biological detection devices, light emitting diodes (LED), phosphors, and photovoltaic solar cells.[1,2] While examples of light emitting semiconductors such as doped metal sulfides[3] and oxysulfides,[4] metal phosphides,[5] etc. are numerous, most suffer from a number of disadvantages. Here we report that metal chalcophosphates can be a promising new class of materials with light emitting properties. Metal chalcophosphates are semiconductors with wide structural diversity[6-8] and many technologically relevant properties such as ferroelectricity,[9] piezoelectricity,[9] nonlinear optical,[10] phase-change,[11] etc. but have not been known to photoluminesce.

Here we report the first examples of photoluminescent chalcophosphates, AZrPS$_6$ [A = K (1), Rb (2, 3), Cs (4)], which exhibit strong red light emission at room temperature. Their emission is not affected by the composition, excitation source, and atmosphere. Radiative near band edge emission in semiconductors is indicative of a direct band gap material. The implications of this emission, when compared to the nonemissive selenophosphate compounds reported previously,[12] could lead to a much better understanding of the atomic electronic and structural interactions that determine the band structure in such complex materials. The long emission lifetimes for these materials we report here suggest a high quality structure that is resilient in air.

Pure compounds could be synthesized and isolated as very small, needle and block shaped single crystals[13] (Figure 1A), for which we successfully determined crystal structure using only Synchrotron radiation (Advanced Photon Source, Argonne National Laboratory). The α-KZrPS$_6$ (1) and α-RbZrPS$_6$ (2) are isostructural to the known α-AZrPSe$_6$ compounds,[12] according to the powder X-ray diffraction patterns.[14] Compounds β-RbZrPS$_6$ (3) and β-CsZrPS$_6$ (4) are isostructural and crystallize in a new polymorphic form having polar space group P1. The single crystal structural data were collected and solved[15] for compound 3 which is shown in Figure 1B. The interactions between the Rb$^+$ ion and the $^1/_\infty$[ZrPS$_6$]$^-$ anions are purely electrostatic and should be weak. The chains have Zr$^{4+}$ centers coordinated to S atoms in a distorted bicapped trigonal prismatic geometry, Figure 1C. All Zr$^{4+}$ ions are connected to a $^1/_\infty$[PS$_3^-$] polymeric backbone which is formed by the condensation of corner-sharing tetrahedral PS$_4$ units, Figure 1D. The PS$_4$ tetrahedron is slightly distorted from the ideal geometry having S−P−S angles ranging from 98.6(8)° to 120(2)°. All the P−S bond lengths are normal at 2.078(15)−2.228(15) Å and 1.862(19) Å for bridging and terminal bonds respectively. The Zr atoms are also bridged with η$^4$-bonded S$_2^{2-}$ groups to form a straight Zr···Zr···Zr

column with an equal Zr---Zr distance of 3.614(2) Å. The S−S bond length in S$_2^{2-}$ is 2.146(10) Å. The prisms formed by Zr and S atoms share their trigonal faces and form a column of prisms along the spine of the polymeric chain running along the *a*-axis of the unit cell, Figure 1C. In addition, each Zr atom has a terminal S atom attached to it.
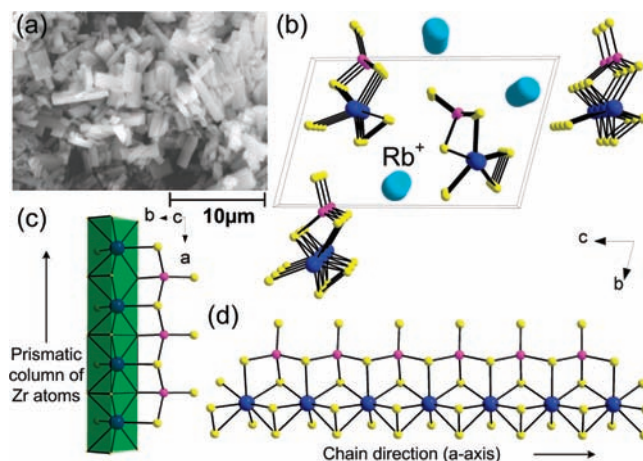


**Figure 1.** (A) SEM image of rod shaped microcrystals of KZrPS$_6$. (B) Noncentrosymmetric structure of β-RbZrPS$_6$ (3). View along the [100] direction. Color code: Zr, Dark Blue; S, Yellow; P, Pink. (C) Projection view showing the column of prismatic Zr atoms, the trigonal prismatic geometry is shown by face-sharing green polyhedra. (D) Polymeric $^1/_\infty$[PS$_3^-$] chain acting as a backbone holding the Zr$^{4+}$ ions together.

The electronic absorption spectra for AZrPS$_6$ compounds showed a very steep and strong absorption edge at ∼2.1 eV, Figure 2A. The optical absorption spectra likely originate from band gap excitations from a chalcogen atom *p*-orbital based valence band to an empty predominantly *d* orbital of a Zr$^{4+}$ based conduction band. Changes in the alkali metal did not show a major effect on the band gap, mainly because of the nondirectional ionic interactions of alkali metal cations with the $^1/_\infty$[ ZrPS$_6^-$].

The Raman spectra for all four thiophosphate compounds show characteristic strong peaks, Figure 2B. The strong peaks around 420 cm$^{-1}$ and 470 cm$^{-1}$ are from the A$_1$ symmetric stretch of the tetrahedral [PS$_4$]$^{3-}$ unit, whereas the peaks around 260−300 cm$^{-1}$ arise from the P−S bending vibrations in the PS$_4$ unit. All other peaks below 250 cm$^{-1}$ are due to Zr−S bond stretching vibrations. The presence of disulfide (S$_2^{2-}$) bonds in the thiophosphates is confirmed by the appearance of intense peaks around 490−520 cm$^{-1}$.[16] Differential thermal analysis (DTA) showed that all AZrPS$_6$ compounds melt incongruently at 470 °C. The melts recrystallize between 380 and 402 °C.[14]

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The AZrPS$_6$ exhibit strong solid state photoluminescence (PL) at room temperature and emit red light when photoexcited above the band gap. Room temperature red-emitting inorganic phosphor materials are relevant to solid state lighting, photovoltaic cells, radiation sensors, electroluminescent devices, etc.[17] The light emission from these materials near their band gap wavelength suggests that AZrPS$_6$ compounds are direct band gap materials. Also, the light emission from AZrPS$_6$ is independent of the alkali metal cations present in the compound.[14]
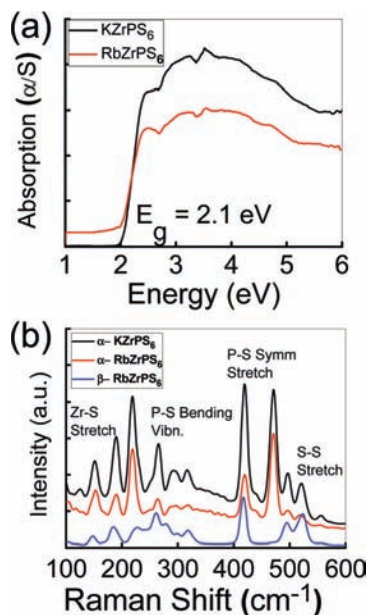


**Figure 2.** (A) Solid-state UV−visible optical absorption spectra of AZrPS$_6$ compounds showing sharp absorption edge at 2.1 eV. (B) Raman spectra of crystalline AZrPS$_6$ compounds showing characteristic shifts.

The emission spectra of α-KZrPS$_6$ (**1**), β-RbZrPS$_6$ (**3**), and β-CsZrPS$_6$ (**4**) are shown in Figure 3A. The spectral width is roughly 230 meV at full width half-maximum (fwhm). Because of the asymmetric spectral line shape and sublinear dependence of the integrated emission intensity on the excitation intensity, the signal is attributed to a donor−acceptor pair recombination.[18,19] The PL decay lifetimes were measured using a "time correlated single photon counting (TCSPC)" technique, to determine the lifetime of the carriers. The PL decay curves for β-RbZrPS$_6$ (**3**) and β-CsZrPS$_6$ (**4**) are shown in Figure 3B. The signal was stable for days upon excitation. At these fluences, the carriers undergo a density-dependent bimolecular decay at earlier times and later the carriers undergo unimolecular decay. This mechanism closely resembles a bimolecular recombination process model with carrier trapping.[20,21] The recombination lifetime of compounds **4** and **3** are 250 and 110 ns, respectively. Compound **1** has a decay time of less than 100 ns. The photoluminescence lifetime of semiconductor materials can vary from picoseconds to milliseconds depending on various characteristics of the materials such as doping density, surface defects, carrier concentration, and defect state levels.[22] The lifetimes for the AZrPS$_6$ compounds are similar to the 150 ns recombination lifetime recorded for high quality Cu(In,Ga)Se$_2$ thin films.[23] In these experiments, the recombination lifetime decreased to less than 300 ps for Cu(In,Ga)Se$_2$ thin films exposed to air. For the latter it was proposed that the oxygen or water in the air creates deep level defect sites in the material, which can quench the PL.

The emission spectra of all AZrPS$_6$ are energetically similar, which indicates that the electronic band structure does not vary
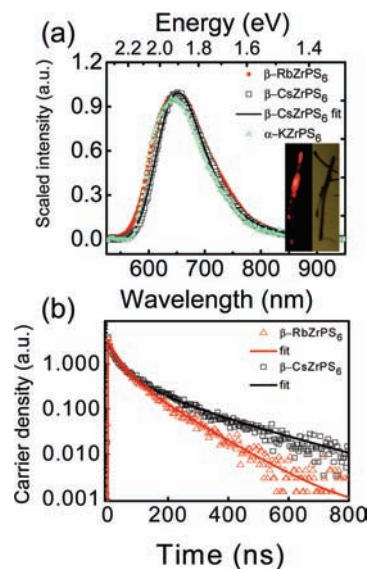


**Figure 3.** (A) Solid state emission spectra for α-KZrPS$_6$ (**1**), β-RbZrPS$_6$ (**3**), β-CsZrPS$_6$ (**4**) compounds. Inset: Real time picture of red light emission from an irradiated solid sample of **1**. (B) Photoluminescence decay traces for crystals of β-RbZrPS$_6$ (**3**) (red) and β-CsZrPS$_6$ (**4**) (black). The laser fluence was ∼100 $\mu$J/cm$^2$. The excitation wavelength was 500 nm, and the emission collection wavelength was 650 nm.

significantly with the alkali cation counterion. Assuming the band structure and donor−acceptor states are similar for these materials, the changes in the recombination lifetime are ascribed to the change in the nonradiative recombination lifetime, which is inversely proportional to the number of nonradiative pathways in the material. The smaller counterion, i.e. K$^+$, could bring the anionic chains close together, which could increase the probability of nonradiative decay which would be consistent with the recombination lifetime trend of K < Rb < Cs discussed above. Also cation specific defects can also affect the recombination lifetime. The stable lifetimes observed in AZrPS$_6$ suggest that these materials are very durable in air.
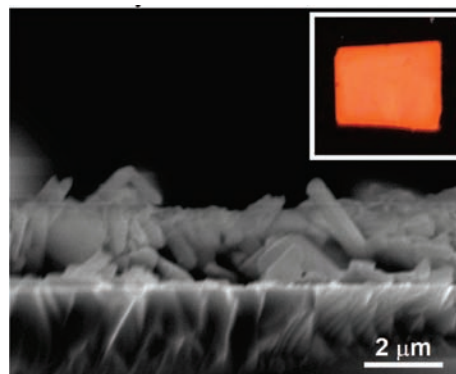


**Figure 4.** Cross-sectional scanning electron micrograph of a KZrPS$_6$ film on Si. Inset: real-size (10 × 8 mm) image of the film. The film was prepared by dispersing 100 $\mu$L of a 10 mg/mL suspension of KZrPS$_6$ in *N,N*-dimethylformamide.

In addition to excellent atmospheric stability, AZrPS$_6$ crystals are quite amenable to solution processing, which is advantageous when considering potential device fabrication. Figure 4 displays a cross-sectional scanning electron micrograph of a thin film prepared by drop-casting a suspension of KZrPS$_6$ in *N,N*-dimethylformamide. The films are very monodisperse over the entire substrate, and the film thickness can be controlled by adjusting the concentration of the suspension. Solution processability is a desirable trait that the

$AZrPS_6$ crystals share with many organic semiconducting materials. We thus have a material that can be easily processed like a semiconducting polymer but also, because of its inorganic nature, can have superior stability, emission, and charge transport characteristics over organic materials. Electrical characterization of these films indicates a room temperature resistivity of $3.5 \times 10^5$ Ohm·cm.

$AZrPS_6$ are unique examples of stable inorganic semiconductors with band gap emission and promising excited state properties for technological applications as photovoltaic and light emitting materials. They are the first thiophosphate compounds which show strong emission at room temperature. The PL lifetimes of $AZrPS_6$ materials are longer compared to many inorganic chalcogenide semiconductors indicative of slower nonradiative pathways during emission and suggesting robust structures that are tolerant to interfering defects. They also suggest reasonable diffusion lengths of photoexcited carriers. Further efforts are under way utilizing these materials in photovoltaic and light emitting devices.[24]

**Supporting Information Available:** X-ray crystallographic file (in CIF format) as well as tables for structural information. This material is available free of charge via the Internet at http://pubs.acs.org.

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(13) α-KZrPS₆ (**1**) and α-RbZrPS₆ (**2**): In a nitrogen-filled glovebox, $K_2S$/$Rb_2S$, Zr, $P_2S_5$, and S were loaded in 2:1:2:6 molar ratios in a 9 mm quartz tube and was sealed under vacuum ($\sim 8 \times 10^{-4}$ mbar). Then the reaction mixture was heated at 500 °C for 72 h followed by cooling to 350 °C in 72 h and to 295 °C in 36 h and finally to room temperature in 3 h. The yellow-orange colored melt was then taken out of the tube and dissolved in degassed $N,N'$-dimethylformamide. Microneedle shaped orange colored crystals (yield >70%) were isolated after washing with ether. β-RbZrPS₆ (**3**) and β-CsZrPS₆ (**4**): In a nitrogen-filled glovebox, $Rb_2S$/$Cs_2S$, Zr, $P_2S_5$, and S were loaded in 2:1:2:10 molar ratios as described above. Then the reaction mixture was heated at 900 °C for 72 h followed by cooling to 300 °C in 60 h and finally to room temperature in 3 h. The orange colored melt was then taken out of the tube and dissolved in degassed $N,N'$-dimethylformamide. Microneedle shaped orange crystals (yield >70%) were isolated after washing with ether.

(14) Supporting Information.

(15) Single crystal diffraction data were collected using the Synchrotron radiation source at Advanced Photon Source at the Argonne National Laboratory. An APEX2 detector was used and data were collected using a $\varphi$-scan technique at two arbitrary omega positions. Diamond monochromatized synchrotron radiation was used. Data reduction was performed with the APEX2 software, SAINT and SADABS. Crystal Structure Data for β-RbZrPS₆ (**3**): Triclinic; $P\bar{1}$; $Z = 2$; $a = 3.5979(19)$ Å, $b = 9.064(5)$ Å, $c = 14.452(8)$ Å, $\alpha = 75.267(13)°$, $\beta = 83.602(9)°$, $\gamma = 87.354(9)°$, $V = 452.9(4)$ Å³. Crystal size: $2 \times 2 \times 15$ $\mu m^3$; $T = 298(3)$ K; $2\theta$ range: 0.91° to 17.66°; $D_{calc} = 2.9322$ g/cm³; $F(000) = 376$; Index ranges: $-2 \leq h \leq 4, -11 \leq k \leq 11, -19 \leq l \leq 17$; Reflections collected = 4580, Independent reflections = 2390 [$R_{int} = 0.069$]; Completeness to $\theta = 15.56° = 98\%$; Data/restraints/parameters = 1824/0/99; Final $R$ indices [$I > 3\sigma(I)$]: $R_{obs} = 0.083$, $wR_{obs} = 0.178$. In addition to the small size the crystals were also found heavily twinned. Two non-merohedral twin domains were separated during integration, and the reflections from one domain were used. An additional merohedral twin law of an 180° rotation along the 011 axis [$-1 -0.379 -0.379\ 0\ 0.557\ 1.557\ 0\ 0.443 -0.557$] was used during the structure solution with a refined fraction of 48.1(6)%. The structure of **3** was refined using JANA2006 (Petricek, V., Dusek, M., Palatinus, L. *JANA 2006: The crystallographic computing system*; Institute of Physics, Praha, Czech Republic, 2006).

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