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Communication

$K_3Ln(AsS_4)_2$ (Ln = Nd, Sm, Gd): the First Rare Earth Thioarsenate Compounds with Infinite Straight $^1_\infty[Ln(AsS_4)_2]^{3-}$ Chains

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The structures of the novel compounds $K_3Ln(AsS_4)_2$ (Ln = Nd, Sm, Gd) contain infinite straight $^1_\infty[Ln(AsS_4)_2]^{3-}$ anionic chains which are composed of interconnected LnS_8 polyhedra and AsS_4 tetrahedra. The compounds were synthesized via reactions of Ln metals with in-situ-formed potassium polythioarsenate fluxes.

Many quaterny chalcogenoarsenates of alkali, main goup, and transition metals with various structures have been reported in the past.[1−13] The considerable structural variation in these compounds is due to the stereochemical active lone pair electrons of As(III). Along with the variable coordinative character of $[As_xQ_y]^{n-}$ anions, it is expected that new compounds with a complicated struture will be generated by applying large electropositive cations such as lanthanides (RE) in the syntheses. The large size and high coordination numbers of RE elements may lead to special metal−chalcogen bonding characters.

Compared to the broad information now available on the reactivity of RE elements in molten alkali metal polychalcophosphate and -antimonate fluxes,[14−29] no such information is available about RE polyarsenates. An interesting question is whether As is found in the oxidation state +5 and forms compounds with structures reminiscent to that of chalcogenophosphates, or if As adopts the chemistry of chalcogenoantimonites. Comparing the properties of P, As, and Sb there seems to be a boundary at As in terms of the chemical and electronic behavior. The most stable oxidation states of P are +4 and +5, as evidenced by the frequent occurrence of $[P_2Q_6]^{4-}$ [12] and $[PQ_4]$ building units^{3-} [8] (Q = S, Se). These oxidation states are not likely for Sb due to the greater stability of the +3 oxidation state in the presence of S or Se, and no $Sb(IV)S_x$ unit has been reported so far. The ethane-like units $[As_2Q_6]^{4-}$ and $[Sb_2Q_6]^{4-}$ do not exist. Therefore, we anticipate a contrast among the $[P_xQ_y]^{n-}$, $[As_xQ_y]^{n-}$, and $[Sb_xQ_y]^{n-}$ chemistry.

In this communication, we report on the reactivity of Ln (Ln = Nd, Sm, Gd) metals in potassium thioarsenate melts and the characterization of the isostructural compounds $K_3Ln(AsS_4)_2$, the first series of compounds with a structure containing infinite straight anionic chains composed of interconnection of AsS_4^{3-} tetrahedra.

The compounds $K_3Ln(AsS_4)_2$ were obtained as light yellow or colorless transparent needles in potassium polythioarsenate fluxes of relative low Lewis basicity or sulfur-rich flux (formally “$K_2As_2S_{12}$”).[30] These compounds are not formed in more basic fluxes, suggesting that low basicity is important for stabilization of the compounds. The products obtained under more basic reaction conditions were also investigated. Applying a flux with a molar ratio of 2:1:6 for $K_2S_3/As_2S_3/S$

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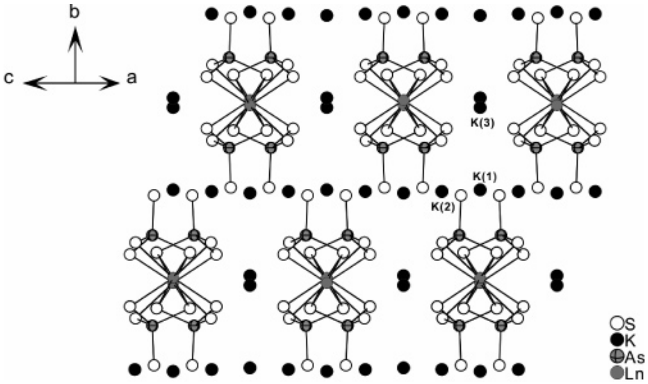

Figure 1. View of the structure of $K_3Ln(AsS_4)_2$ along [101] showing $^1_\infty[Ln(AsS_4)_2]^{3-}$ chains separated by potassium atoms. Selected bond lengths (in Å): $K_3Nd(AsS_4)_2$: Nd(1)−S(2) 2.854(1), Nd(1)−S(4) 2.880(1), Nd(1)−S(3) 3.045(1), 3.093(1), As(1)−S(1) 2.126(1), As(1)−S(2) 2.166(1), As(1)−S(4) 2.169(1), As(1)−S(3) 2.176(1). $K_3Sm(AsS_4)_2$: Sm(1)−S(2) 2.824(1), Sm(1)−S(4) 2.853(1), Sm(1)−S(3) 3.037(1), 3.086(1), As(1)−S(1) 2.127(1), As(1)−S(2) 2.169(1), As(1)−S(4) 2.171(1), As(1)−S(3) 2.177(1). $K_3Gd(AsS_4)_2$: Gd(1)−S(2) 2.799(1), Gd(1)−S(4) 2.830(1), Gd(1)−S(3) 3.022(1), 3.074(1), As(1)−S(1) 2.127(1), As(1)−S(2) 2.167(1), As(1)−S(4) 2.168(1), As(1)−S(3) 2.174(1).

(formal composition of the melt: "$K_4As_2S_{15}$"), the compounds were not formed, and K_3AsS_4, LnS_2, and a variety of K_2S_x phases were identified as main products. Attempts to synthesize $K_3Ln(AsS_4)_2$ from a stoichiometric molar ratio of K_2S_3/Ln/As_2S_3/S were also unsuccessful.

The structure of $K_3Ln(AsS_4)_2$ (Ln = Nd, Sm, Gd) is characterized by the occurrence of infinite $^1_\infty[Ln(AsS_4)_2]^{3-}$ chains propagating along [101].[31] The anionic chains are surrounded by K^+ ions (Figure 1). The chains contain Ln^{3+} cations linked by tridenate $[AsS_4]^{3-}$ ligands (Figure 2a). Each Ln atom is coordinated by four such ligands yielding a distorted bicapped trigonal prism (Figure 2b). Each $[AsS_4]^{3-}$ ligand coordinates to two neighboring Ln centers employing one S atom for each Ln and a third S atom acting as a bridge to both Ln atoms. The fourth S atom remains terminal. The LnS_8 polyhedra share edges along the direction of the chain. A similar structural motif has been observed in rare earth selenophosphates such as $Rb_3Ce(PSe_4)_2$ and $Cs_3Gd(PSe_4)_2$.[23] The difference is that in these selenophosphates alternating short−long−short Ln−Ln distances occur in the chains, whereas in the title compounds all Ln−Ln distances within the chains are identical (5.078(1) Å for Nd−Nd; 5.070(1) Å for Sm−Sm; 5.053(1) Å for Gd−Gd). The average Ln−S distances at 2.97 Å for Nd−S, 2.95 Å for Sm−S, and 2.93 Å for Gd−S compare well with those found in $K_2NdP_2S_7$,[32] $KSmP_2S_6$,[17] and $Ba_3GdP_4S_{16}$.[33] The As−S bond lengths range from 2.126(1) to 2.176(1) Å in $K_3Nd(AsS_4)_2$; (Sm: 2.127(1)−2.177(1) Å; Gd: 2.127(1)−2.174(2) Å) with the terminal sulfur atoms displaying the shorter distances. The three unique K^+ ions are coordinated by eight S atoms ($K_3Nd(AsS_4)_2$: range K(1)−S: 3.209(1)−3.504(2) Å; K(2)−S: 3.119(1)−3.779(1) Å; K(3)−S: 3.223(2)−3.461(1) Å; $K_3Sm(AsS_4)_2$: K(1)−S: 3.199(1)−3.512(1) Å; K(2)−S: 3.123(1)−3.767(1) Å; K(3)−S: 3.232(1)−3.443(1) Å; $K_3Gd(AsS_4)_2$: K(1)−S: 3.182(2)−3.498(2) Å; K(2)−S: 3.120(2)−3.755(2) Å; K(3)−S: 3.232(2)−3.425(2) Å;). Compared to title compounds, there are also three different Rb sites in $Rb_3Ce(PSe_4)_2$ and $Cs_3Gd(PSe_4)_2$,[23] but the coordination number of Rb(3) is six whereas those of Rb(1) and Rb(2) are eight. The shortest interchain S−S distances of 4.066(1) Å in $K_3Nd(AsS_4)_2$ (Sm: 4.108(2) Å; Gd: 4.130(3) Å) are much larger than the sum of van der Waals radii of S (3.6 Å). Since there are no S−S interactions in these compounds, the formal oxidation states can be assigned as K(+1), Ln(+3), As(+5), and S(−2). Each chain is surrounded by six other chains in a pseudohexagonal fashion.

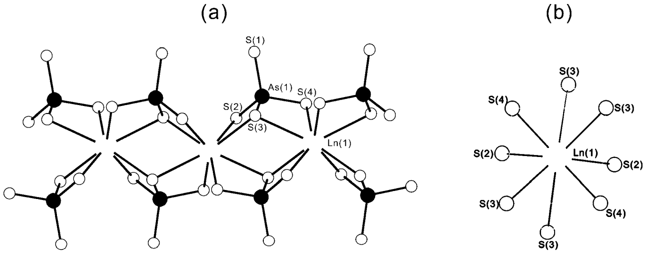

Figure 2. (a) Single chain of $[Ln(AsS_4)_2]$ with labeling scheme. (b) Local coordination environment of Ln atoms.

Among these compounds, solid-state UV/vis/NIR spectroscopy[34] shows that $K_3Sm(AsS_4)_2$ has a relatively steep absorption edge that corresponds to an energy band gap, E_g, of ∼2.2 eV, consistent with its yellow color. The electronic absorption responsible for the gap is likely an electronic charge-transfer excitation of sulfur-based p orbitals to vacant Sm d orbitals. The Raman spectrum[35] obtained on a single

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(30) All operations were carried out in a nitrogen-filled glovebox. K_2S_3, Ln (Nd, Sm, Gd), As_2S_3, and S in a 1:1:1:6 molar ratio were thoroughly mixed. The mixtures were then loaded into 6 mm silica tubes which were subsequently evacuated (∼2 × 10^{-3} mbar) and flame sealed. The tubes were heated from 25 to 600 °C within 24 h and kept at this temperature for 4−5 days, and cooled to 100 °C at a rate of 3 °C/h followed by cooling to room temperature in 4 h. The resulting black melt was washed with DMF and acetone, and the product was dried in a vacuum. Moisture-sensitive, light yellow or colorless transparent needle crystals of $K_3Ln(AsS_4)_2$ (Ln = Nd, Sm, Gd) (50∼60%) were isolated by washing away the excessive flux with *N*,*N*-dimethylformamide. Energy-dispersive X-ray analyses (EDX) on a number of crystals indicated the presence of K, Ln, As, S in an ∼3:1:2:8 molar ratio.

(31) Single-crystal X-ray diffraction intensity data were collected on a Stoe imaging plate diffraction system (IPDS-1) with graphite-monochromatized Mo Kα radiation. The crystals were manually selected from the reaction products and mounted on the top of glass fibers and bathed in cold nitrogen stream during data collections. Numerical absorption corrections were applied to the data using X-Shape and X-red based on face indexing. All three compounds crystallize in space group *C*2/*c* (No. 15). Crystal data: (a) $K_3Nd(AsS_4)_2$: $a = 10.3736(8)$ Å, $b = 18.8768(13)$ Å, $c = 8.8393(7)$ Å, $\beta = 116.878(8)°$, $V = 1543.9(2)$ Å^3, $Z = 4$, $T = 180$ K, R1(F) = 0.0281, wR2(F^2) = 0.0682, GOF = 1.000. (b) $K_3Sm(AsS_4)_2$: $a = 10.3741(9)$ Å, $b = 18.8228(14)$ Å, $c = 8.8484(7)$ Å, $\beta = 117.013(9)°$, $V = 1539.3(2)$ Å^3, $Z = 4$, $T = 220$ K, R1(F) = 0.0266, wR2(F^2) = 0.0657, GOF = 0.990. (c) $K_3Gd(AsS_4)_2$: $a = 10.3484(7)$ Å, $b = 18.8039(14)$ Å, $c = 8.8238(6)$ Å, $\beta = 117.063(7)°$, $V = 1529.0(2)$ Å^3, $Z = 4$, $T = 220$ K, R1(F) = 0.0351, wR2(F^2) = 0.0823, GOF = 0.974.

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(34) UV/vis/NIR diffuse reflectance spectra were recorded on a Cary 5 spectrometer (Varian Techtron Pty.). The spectrometer was equipped with an Ulbricht sphere (diffuse reflectance accessory; Varian Techtron Pty.). The samples were ground together with $BaSO_4$ and prepared as a flat specimen of ∼2 mm thickness. Resolution was 1 nm for the UV/vis range and 2 nm for the near-IR range. The measuring range was 250−2000 nm. $BaSO_4$ was used as a standard for 100% reflectance.

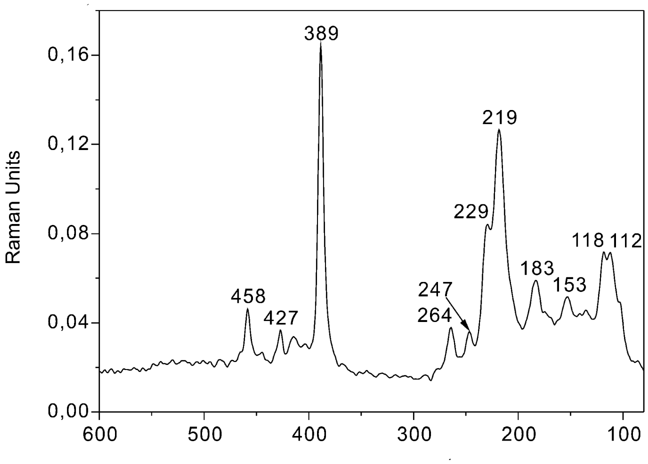

Figure 3. Fourier transform Raman spectrum of $K_3Sm(AsS_4)_2$.

crystal of $K_3Sm(AsS_4)_2$ exhibits a very strong peak at 389 cm^{-1} together with some weak bands (Figure 3) which are assigned to the stretching and deformation modes of the $[AsS_4]^{3-}$ anion. These values are shifted to lower energies compared with those of thiophosphates due to the larger mass of As.

In the contribution we presented the first RE chalcoarsenate compounds. Furthermore, we have shown that changing the composition or Lewis basicity of the flux the reactivity of Ln and the outcome of the reaction can be controlled. Namely, the compounds $K_3Ln(AsS_4)_2$ were successfully synthesized in sulfur-rich potassium polyarsenate flux with a relatively low Lewis basicity. These conditions seem to be essential for the stabilization of these compounds because increasing the flux basicity results in the breakdown of the structures and formation of simpler compounds.

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Supporting Information Available: X-ray crystallographic files in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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(35) Fourier transform Raman spectrum was recorded on an ISF-66 spectrometer (Bruker) with additional FRA 106 Raman module. A Nd:YAG laser was used as source of excitation ($\lambda = 1064$ nm). The samples were ground and prepared on Al sample holders. The measuring range was -1000 to 3500 cm^{-1} with a resolution of 2 cm^{-1}.