Poster

$Rb_4[As_2S_{10}]$: A Rubidium Polythioarsenate(V) with an Unusual Discrete $[S_3AsS(S_2)SAsS_3]^{4-}$ Anion

Katja Engel[1], Thomas Schleid[1]

[1]*Institute for Inorganic Chemistry, University of Stuttgart, Germany*
schleid@iac.uni-stuttgart.de

Since polythioarsenate and -phosphate fluxes were successfully used during the syntheses of quaternary thioarsenates and -phosphates in the past, it is surprising that for thioarsenates just a few $[As_xS_y]^{n-}$ anions such as $[AsS_4]^{3-}$ and $[AsS_3]^{3-}$ are known [1,2]. In an attempt to expand the diversity of those thioarsenates, $Rb_4[As_2S_{10}]$ as the first alkali-metal polythioarsenate(V) including discrete $[S_3AsS(S_2)SAsS_3]^{4-}$ anions occurred.

$Rb_4[As_2S_{10}]$ was synthesized from a mixture of Rb_2S:As_2S_5:S in a molar ratio of 2:1:7, which was heated up to 500 °C in a glassy silica ampoule. Single-crystal XRD shows that $Rb_4[As_2S_{10}]$ crystallizes monoclinically in the space group $P2_1/c$ with a = 1735.21(9) pm, b = 699.36(4) pm, c = 2355.83(12) pm and β = 93.975(3)° for Z = 6 (CSD number: 2350774). The crystal structure is characterized by discrete $[As_2S_{10}]^{4-}$ units, so far unknown for arsenic compounds, separated by Rb^+ cations with *C.N.*(Rb^+) = 8 – 10. These anions are built by two $[AsS_4]^{3-}$ tetrahedra linked by two sulfur atoms forming a tetrasulfide chain fragment $(S_4)^{2-}$ in the center of each $[S_3AsS(S_2)SAsS_3]^{4-}$ entity. This As^{5+}-bridging chain occurs in different conformations, since the torsion angle in $[(As1)(As2)S_{10}]^{4-}$ equals 89.7°, but is 180° for $[(As3)_2S_{10}]^{4-}$. Compared with similar polythiophosphates(V) $A_4[P_2S_{10}]$ (A = Rb, Cs), the crystal structure differs with respect to the connecting tetrasulfide chain fragments [3,4]. While for the thiophosphates the chain in $[(Pn3)_2S_{10}]^{4-}$ (Pn = P and As) is reported to have unequally occupied split positions [3,4], the crystal structure of $Rb_4[As_2S_{10}]$ appears to be well ordered. The corresponding Raman spectrum is very unique and could be used as a fingerprint. The optical band gap of $Rb_4[As_2S_{10}]$ was calculated to be 2.48 eV.

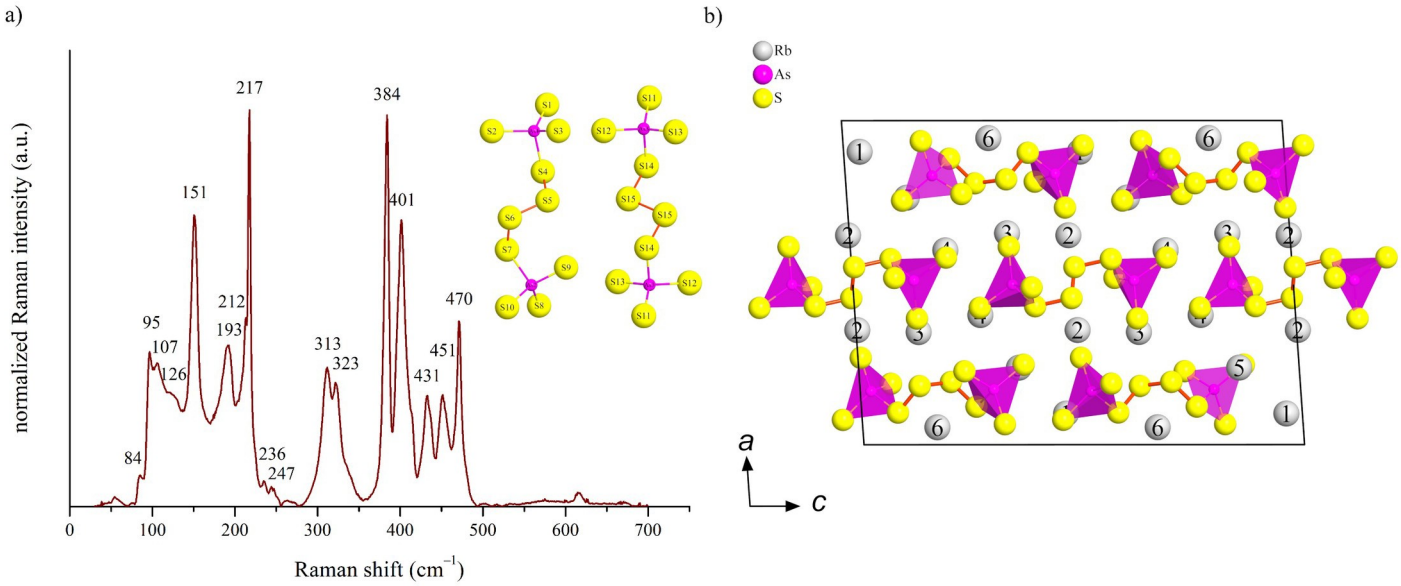

Figure 1. Raman spectrum of $Rb_4[As_2S_{10}]$ with two structurally different $[As_2S_{10}]^{4-}$ units (a, *left*) and unit-cell content with highlighted $[As_2S_{10}]^{4-}$ anions (b, *right*).

[1] Bera, T. K., Kanatzidis, M. G. (2008). *Inorg. Chem.* **47**, 7068.

[2] Wu, Y., Näther, C., Bensch, W. (2006). *Inorg. Chem.* **45**, 8835.

[3] Aitken, J. A., Canlas, C., Weliky, D. P., Kanatzidis, M. G. (2001). *Inorg. Chem.* **40**, 6496.

[4] Alahmari, F., Davaasuren, B., Khanderi, J., Rothenberger, A. (2016). *Z. Anorg. Allg. Chem.* **642**, 361.