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Aluminosilicate Relatives: Chalcogenoaluminogermanates $Rb_3(AlQ_2)_3(GeQ_2)_7$ (Q = S, Se)

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The new compounds $Rb_3(AlQ_2)_3(GeQ_2)_7$ [Q = S (**1**), Se (**2**)] feature the 3D anionic open framework $[(AlQ_2)_3(GeQ_2)_7]^{3-}$ in which aluminum and germanium share tetrahedral coordination sites. Rb ions are located in channels formed by the connection of 8, 10, and 16 $(Ge/Al)S_4$ tetrahedra. The isostructural sulfur and selenium derivatives crystallize in the space group $P2_1/c$. **1**: a = 6.7537(3) Å, b = 37.7825(19) Å, c = 6.7515(3) Å, and β = 90.655(4)°. **2**: a = 7.0580(5) Å, b = 39.419(2) Å, c = 7.0412(4) Å, β = 90.360(5)°, and Z = 2 at 190(2) K. The band gaps of the congruently melting chalcogenogermanates are 3.1 eV (**1**) and 2.4 eV (**2**).

Thio- and selenogermanates are a well-known class of compounds with a rich structural chemistry and numerous known minerals.[1] They feature a diverse set of building blocks such as the tetrahedral $[GeQ_4]^{4-}$,[2] the ethane-like $[Ge_2Q_6]^{6-}$,[3] edge-sharing tetrahedra $[Ge_2Q_6]^{4-}$,[4] $[Ge_2Q_7]^{6-}$ formed by corner-sharing $[GeQ_4]$ tetrahedra,[5] the adamantane $[Ge_4Q_{10}]^{4-}$,[6] and a variety of other architectures including $[GeQ_3]^{2-}$ chains,[7] lamellar $[Ge_2Q_5]^{2-}$ solids, and $[Ge_4Q_{10}]^{8-}$ rings (Q = S, Se).[3b,7,8] Chalcogenogermanates have been synthesized in the form of templated mesostructured arrangements[9] with gas-separation applications.[10] Noncentrosymmetric chalcogenogermanates are potential nonlinear optical (NLO) materials,[11] as well as ferroelectric[2b] and thermoelectric materials.[12]

Commonly, chalcogenogermanates are prepared in polychalcogenide and [13] metal halide fluxes[14] and by direct combination reactions or solvothermal methods.[4a,15] Here we describe the construction of anionic chalcogenogermanate frameworks by mixing germanium with aluminum in order to build a negatively charged arrangement composed of connected $[Ge_xAl_{1-x}Q_4]$ tetrahedra. The diagonal relationship of aluminum and germanium describing the similar ionic radii of Al^{3+} and Ge^{4+} should allow a homgeneous distribution of aluminum within a chalcogenogermanate framework.[16] This synthetic strategy has been applied extensively in the synthesis of porous aluminogermanates and aluminosilicates (zeolites).[17] In aluminosilicate minerals and zeolites, the ratio SiO_2/Al_2O_3 is 2 (type A), 2.0−3.0 (type X), and >3.0−6.0 (type Y). Chalcogenides with group 14/13 element ratios similar to those observed in zeolites are therefore a viable

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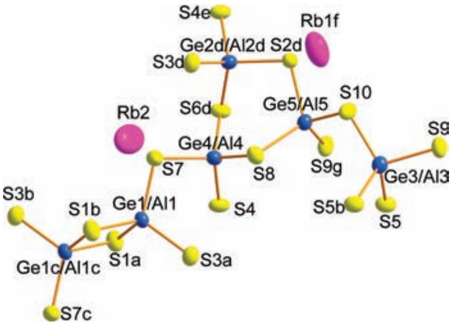

Figure 1. Section of the 3D chalcogenoaluminogermanate framework in **1** showing both corner- and edge-sharing (Ge/Al)S_4 tetrahedra (ellipsoids at the 80% probability level). Atoms having a letter behind the atom number are symmetry-generated. Ge/Al−S bond distances are ca. 2.2 Å. The approximate Ge/Al ratios are Ge1:Al1 = 0.75:0.25, Ge2:Al2 = 0.8:0.2, Ge3:Al3 = 0.7:0.3, Ge4:Al4 = 0.5:0, and Ge5:Al5 = 0.75:0.25.

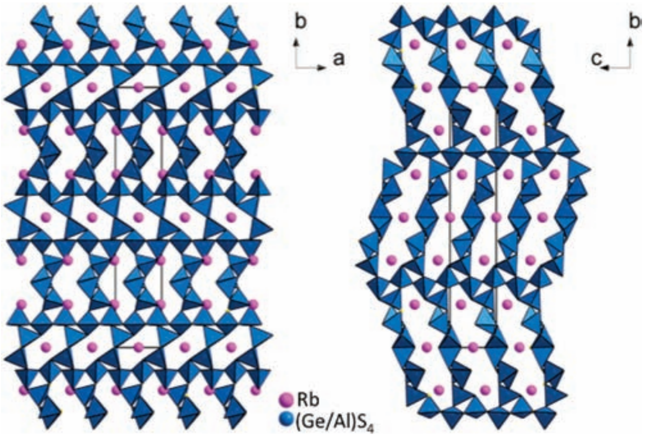

Figure 2. Packing diagram of **1** showing two views of the unit cell within the 3D thioaluminogermanate framework. The different channels within the thioaluminogermanate are occupied by Rb ions. The length of the pore in the (100) plane is ca. 2 nm.

synthetic target.[17b] So far, examples for group 13 metal chalcogenogermanates are rare. Only recently were the promising NLO material $Li_2Ga_2GeS_6$,[11b] which exhibits a 3D-connected network of ordered GeS_4 and GaS_4 tetrahedra, and the layered $KMGeS_4$ (M = In, Ga)[18] reported. As a contribution to this area, we here report the synthesis of the chalcogenoalumogermanates $Rb_3(AlQ_2)_3(GeQ_2)_7$ [Q = S (**1**), Se (**2**)]. Because both $Rb_3(AlS_2)_3(GeS_2)_7$ (**1**) and $Rb_3(AlSe_2)_3(GeSe_2)_7$ (**2**) are isostructural, only **1** will be discussed in detail (Figure 1).[19,20]

Energy-dispersive X-ray (EDX) of crystals of **1** revealed a composition of ca. “$RbAlGe_2S_6$”, which is close to the true composition $Rb_3Al_3Ge_7S_{20}$ (**1**), which was determined by X-ray analysis. The thioaluminogermanate **1** crystallizes in the monoclinic space group $P2_1/c$. $Rb_3(AlS_2)_3(GeS_2)_7$, which is a more descriptive formulation of **1**, consists of the new 3D polymeric framework $[(AlS_2)_3(GeS_2)_7]^{3-}$, in which Al and Ge atoms share positions. The overall Al/Ge ratio is determined by the presence of three Rb cations per formula unit.

The large thermal ellipsoids of the Rb atoms, however, could suggest partial occupancy and less anionic charge $[Rb_x(AlS_2)_x(GeS_2)_7, x < 3]$. In order to verify the Al/Ge ratio on each tetrahedral coordination site, free variables were used in the initial refinement, giving the exact ratio of Al:Ge as 2:7. These free variables were later taken and used as constants in the refinement (xyz and U_{ij} were equated using the “exyz” and “eadp” instructions).[21] The slightly elongated thermal ellipsoids for Rb ions are due to some unresolved disorder/mobility in the cavities of the structure and are not due to partial occupancy. The Rb ions in **1** only form weak electrostatic contacts with surrounding S atoms (Rb−S ca. 3.4−3.8 Å). The tetrahedral (Ge/Al)S_4 building blocks are connected into an elaborate 3D network consisting of corner- and edge-sharing tetrahedra. Rb ions are located within the channels formed. The connected tetrahedra form rings that consist of eight (Ge/Al)S_4 units (one Rb atom is located in the middle; Figure 2, left). The v-shaped void (Figure 2, left; containing two Rb ions) is the result of 10 corner-sharing (Ge/Al)S_4 tetrahedra, and the uniform channels in the [100] direction are formed by 16 (Ge/Al)S_4 units (2 × 8 corner-sharing tetrahedra connected via edge-sharing terminal tetrahedra; Figure 2, right). **1** is *not* analogous to aluminosilicate zeolites: There are the 4-connected tetrahedral framework and the extra-framework cations that are located in voids or channels, but because of the synthetic conditions, there is no adsorbed phase (water in the case of zeolites).

We have undertaken studies regarding the structural and chemical stability of the framework. Preliminary results indicate that **1** is formed even when the ratio of Al:Ge is varied. Compound **1** is partially hydrolyzed when suspended in water at room temperature to give a colorless solid (EDX: Rb:Al:Ge:S = 1:2:2:3.5; the powder X-ray diffraction pattern recorded after **1** was suspended in water for 2 days showed unreacted **1** and several oxides; see the Supporting Information). These initial findings have implications on the synthesis of compounds related to **1**. Because of the slow hydrolysis of **1** in water, hydrothermal conditions do not seem to be suitable for the synthesis of thioaluminogermanates similar to **1**. **1** is thermally stable (Figure 3a) and loses only 1.5 wt % when heated up to 600 °C (Figure 3a). The differential thermal analysis showed that **1** melts at 873 °C and crystallizes at ca. 820 °C (Figure 3b).

The powder X-ray diffraction pattern of **1** was in good agreement with a simulated pattern from single-crystal X-ray diffraction data before and after the differential thermal

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[19] The synthesis of **1** was achieved by heating stoichiometric amounts of Rb_2S_5, Al, Ge, and S in a sealed and evacuated fused-silica tube at 850 °C for 3 days and cooling to 400 °C in 4 days (quantitative yield). Compound **2** was synthesized in an analogous manner using Rb_2Se. **2** was formed together with a black amorphous byproduct (EDX: Al, 4 atom %; Ge, 26 atom %; Se, 64 atom %; Rb, 6 atom %).

[20] Crystal data for **1**: $Rb_3Al_3Ge_7S_{20}$, a = 6.7537(3) Å, b = 37.7825(19) Å, c = 6.7515(3) Å, β = 90.655(4)°, V = 1772.68(14) Å^3, Z = 2, M = 1486.68 g mol^{-1}, $P2_1/c$ (No. 14), T = 190(2) K, λ = 0.71 Å, D_{calcd} = 2.866 g cm^{-3}, μ = 11.527 mm^{-1}, R1 [$I > 2\sigma(I)$] = 0.0242, wR2 = 0.0543. Crystal data for **2**: $Rb_3Al_3Ge_7Se_{20}$, a = 7.0580(5) Å, b = 39.419(2) Å, c = 7.0412(4) Å, β = 90.360(5)°, V = 1958.9(2) Å^3, Z = 2, M = 2424.68 g mol^{-1}, $P2_1/c$ (No. 14), T = 293(2) K, λ = 0.710 73 Å, D_{calcd} = 4.111 g cm^{-3}, μ = 27.652 mm^{-1}, R1 [$I > 2\sigma(I)$] = 0.0380, wR2 = 0.0855

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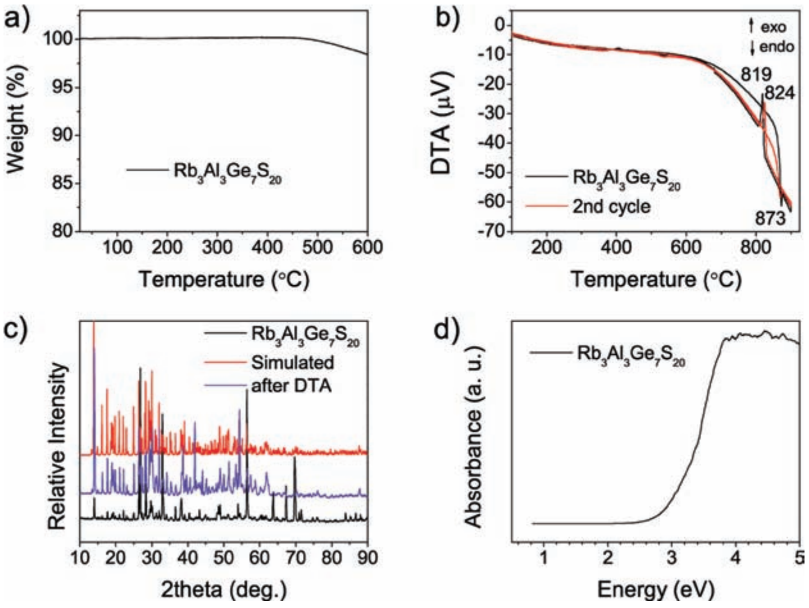

Figure 3. Compound **1**. (a) Thermogravimetric analysis (N_2 flow, heating rate 10 °C min^{-1}). (b) Differential thermal analysis (recorded in sealed quartz ampules (N_2 flow, heating rate 5 °C min^{-1}). (c) Powder X-ray diffraction pattern. (d) UV/vis absorption spectrum.

analysis (Figure 3c) and suggests that **1** melts congruently. Figure 3d shows the solid-state absorption spectra of **1** from which a band gap of ca. 3.1 eV was determined. **2** has a band gap of 2.4 eV. **2** is stable in diluted hydrochloric acid and melts congruently at 730 °C. The preparation of other novel chalcogen derivatives of Ge-based aluminosilicate analogues is currently being explored using Ge/Al mixtures.

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Supporting Information Available: SEM spectra, crystallographic information files (CIF), and characterization of **1** and **2**. This material is available free of charge via the Internet at http://pubs.acs.org.