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Copper-Rich Framework Sulfides: $A_4Cu_8Ge_3S_{12}$ (A = K, Rb) with Cubic Perovskite Structure

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Two copper-rich open-framework sulfides, $K_4Cu_8Ge_3S_{12}$ (**1**) and $Rb_4Cu_8Ge_3S_{12}$ (**2**), have been synthesized under solvothermal conditions. Compounds **1** and **2** are isostructural and contain icosahedral $[Cu_8S_{12}]^{16-}$ clusters as basic building blocks. These clusters are primitive cubic packed and connect to one another by discrete Ge^{4+} ions to generate 3D copper-rich Cu−Ge−S framework and form 3D channels along ⟨100⟩ directions where the alkali metal cations reside. These two open-framework sulfides crystallize in cubic perovskite structure.

Microporous materials with regular pore architectures are important in industrial technologies such as catalysis, sorption, and ion exchange.[1] Since 1989,[2] considerable efforts have been devoted to developing open-framework chalcogenides due to their porosity and intriguing architectures and topologies,[3−12] as well as their potential applications in areas ranging from fast-ion conductivity[6c] to selective ion exchange[7,12] and efficient visible-light photocatalysis.[6e,f,h]

Among the porous metal chalcogenide family, the majority are based on the group 13 and group 14 systems, as well as these systems doped with some transition metal ions, which are featured by tetrahedral coordination of cations.[3−11] In comparison, framework chalcogenides constructed by M^I ($M^I = Cu^+$ or Ag^+) ions represent a unique system in which monovalent cations prefer relative low coordination modes (2, 3) and anions adopt multiple bridging manners (4, 5, 6) to decrease framework negative charge.[13] However, the multiple-bridging manners of anions do not facilitate the construction of open-framework structure.

Our research reveals that the incorporation of high valent Sn^{4+} ions into the Cu^I−S system can balance part of the negative charge and decrease the coordination number of S^{2-} ions to form a more open framework.[14c] On the basis of efforts to explore Cu^+- or Ag^+-containing quarternary chalcogenides,[9,14] we are increasingly interested in incorporating

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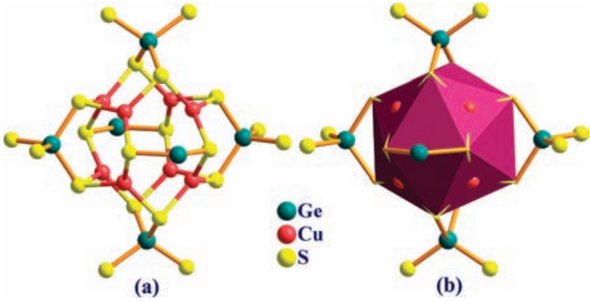

Figure 1. Icosahedral $[Cu_8S_{12}]^{16-}$ cluster and its coordination geometry with six Ge^{4+} ions: (a) ball and stick mode; (b) polyhedral mode.

M^{IV} (M^{IV} = Ge^{4+}, Sn^{4+}) ions with tetrahedral coordination into the M^I−S systems to construct novel copper-rich or silver-rich open frameworks. These structures may provide valuable insights into the condensation behaviors of M^IS_x and $M^{IV}S_4$ polyhedrons and the design of new open frameworks. Furthermore, our interests were also motivated by their potential fast ion conductivity[6c] and visible-light photocatalysis of these materials.[6e,f,h]

Here we report two copper-rich Ge−Cu−S open-framework sulfides, $K_4Cu_8Ge_3S_{12}$ (**1**) and $Rb_4Cu_8Ge_3S_{12}$ (**2**), with high Cu^+/Ge^{4+} molar ratio (Cu^+/Ge^{4+} = 2.67). Compared with the $(H_2en)_2Cu_8Sn_3S_{12}$ open framework,[14c] these two compounds reported here represent another interesting example in which discrete Ge^{4+} ions link high symmetrical Cu−S clusters to form a 3D copper-rich Cu−Ge−S framework.

Compound **1** crystallizes in the cubic space group $Fm\bar{3}c$ and contains a 3D copper-rich Cu−Ge−S open framework.[15] In an anionic framework, each Cu^+ ion lies on 3-fold rotation axes and adopts regular trigonal coordination geometry with the Cu−S bond length of 2.255(4) Å, and each Ge^{4+} ion resides on a $\bar{4}$ symmetry site and is tetrahedrally coordinated to four S^{2-} ions with the Ge−S bond length of 2.237(2) Å. Each S^{2-} ion adopts a μ_3 bridging mode coordinated to a Ge^{4+} and two Cu^+ ions.

The critical building block of **1** is the icosahedral $[Cu_8S_{12}]^{16-}$ cluster,[6f,14c] as shown in Figure 1, which consists of a cubic array of Cu^+ ions bridged by S^{2-} ions, and has an icosahedral shape defined by the 12 bridging S^{2-} ions. The $[Cu_8S_{12}]^{16-}$ cluster behaves like a superoctahedron due to its coordination geometry with adjacent Ge^{4+} ions (Figure 1). Primitive cubic packing of the icosahedral clusters linking together by discrete Ge^{4+} ions give rise to a 3D Cu−Ge−S open framework, forming 3D intersecting channels along ⟨100⟩ directions, in which K^+ ions reside (Figure 2). Such connectivity is similar to $[M(NH_3)_6]Cu_8Sb_3S_{13}]$ (M = Mn, Fe, Ni) in which copper sulfide cores are linked together by antimony centers.[16]

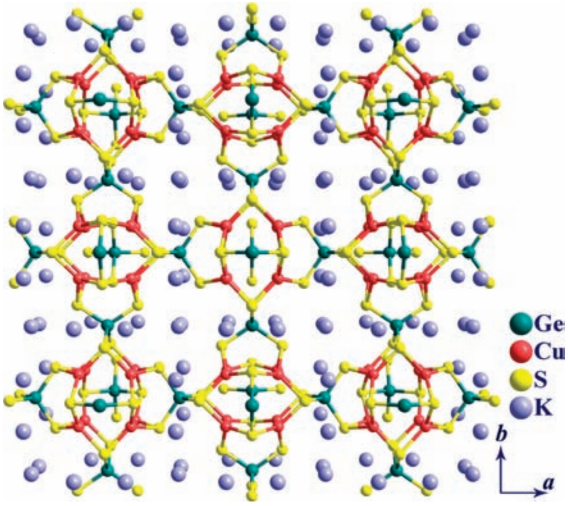

Figure 2. View of the framework of **1** along the *c*-axis.

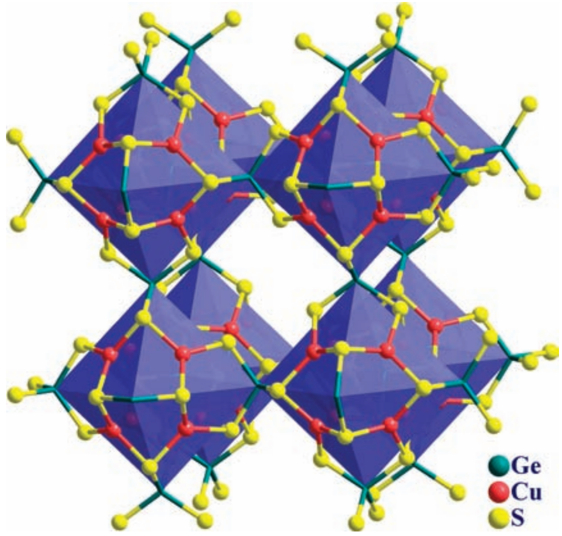

Figure 3. Polyhedral mode of **1** and **2** with cubic perovskite structure (the cations inside are omitted for clarity).

The structure of compound **1** can be derived from cubic perovskite ($CaTiO_3$) type,[17,18] as shown in Figure 3, with $[Cu_8S_{12}]^{16-}$ clusters substituting for octahedrally coordinated Ti^{4+} ions, Ge^{4+} ions substituting for the bridging O^{2-} ions, and four K^+ ions substituting for each Ca^{2+} cation. The four K^+ ions in each cavity are statistically distributed over six equivalent positions, each of which has an occupancy of 2/3. Compound **2** is isostructural with **1**,[15] containing 3D channels in which Rb^+ ions are located.

It is worth comparing these structures with $[Cu_8Ge_5S_{16}]^{4-}$ (**3**) reported recently by Feng et al. which also contains icosahedral $[Cu_8S_{12}]^{16-}$ clusters as building blocks.[6f] In **3**, icosahedral $[Cu_8S_{12}]^{16-}$ clusters are linked by two monomeric

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(15) Data collection was performed on Bruker Smart APEX II diffractometer equipped with graphite monochromitized Mo Kα radiation (λ = 0.71073 Å) at room temperature. The structures were solved by direct methods and refined by full-matrix least-squares on F^2 using the SHELX97. Crystal data for $K_4Cu_8Ge_3S_{12}$ (**1**): cubic, $Fm\bar{3}c$, a = 17.6753 Å, V = 5522.1(9) Å^3, Z = 2, D_c = 3.049 g cm^{-3}, number of reflections = 6143, unique reflections 322 (R_{int} = 0.0554), 262 observed [$I > 2\sigma(I)$], parameters = 15, $R1$ = 0.0426, w$R2$ = 0.1308, GOF = 1.064. CSD-421629. Crystal data for $Rb_4Cu_8Ge_3S_{12}$ (**2**): cubic, $Fm\bar{3}c$, a = 17.5112 Å, V = 5369.7(6) Å^3, Z = 2, D_c = 3.594 g cm^{-3}, number of reflections = 5816, unique reflections 328 (R_{int} = 0.0450), 237 observed [$I > 2\sigma(I)$], parameters = 15, $R1$ = 0.0615, w$R2$ = 0.1806, GOF = 1.037. CSD-421628.

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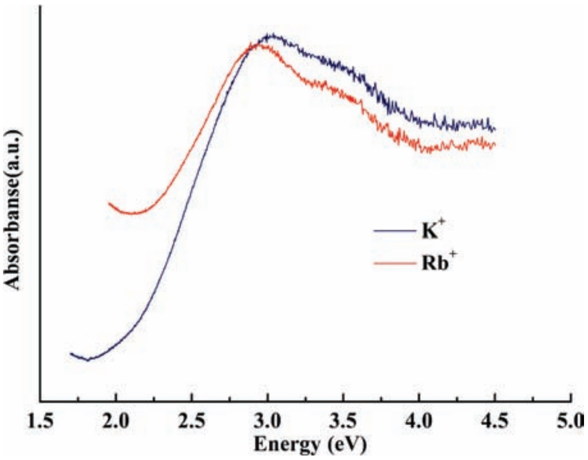

Figure 4. UV−vis reflectance spectroscopy of $A_4Cu_8Ge_3S_{12}$ (A = K^+, Rb^+).

GeS_4^{4-} in the tetragonal *c* direction and four dimeric $Ge_2S_6^{4-}$ units in the *a* and *b* directions to form a 3D framework with tetragonal symmetry, while in **1** and **2**, icosahedral $[Cu_8S_{12}]^{16-}$ clusters are linked by six GeS_4^{4-} units in three directions to form a 3D framework with cubic symmetry. This mainly results from the different size and charge density of the counterions. Compared with the protonated organic amine, K^+ and Rb^+ ions with smaller size and higher charge density are apt to stabilize the framework with higher charge density and less porosity.

The Cu−Ge−S system is interesting because the Cu−S and Ge−S systems can form 3D frameworks independently,[5a,13a,b] and there are many open-framework Cu−Ge−S intermediate phases exhibiting different condensation degrees of Cu−S and Ge−S polyhedrons. Prior to this work, four open-framework Cu−Ge−S phases have been reported.[4,5b,6f] Three of them are low ratio copper-containing Cu−Ge−S open frameworks in which copper ions exist in the form of isolated Cu^+ or Cu_2^{2+} linking $[Ge_4S_{10}]^{4-}$ tetrahedral clusters.[4,5b] With increase of the Cu^I/M^{IV} molar ratio in Cu−Ge−S open frameworks, the condensation degree of Cu−S polyhedrons tends to increase, whereas the condensation of Ge−S polyhedrons tends to be suppressed.[6f] **1** and **2** represent a rare example in which icosahedral $[Cu_8S_{12}]^{16-}$ clusters are present and linked together by discrete GeS_4^{4-} units. The occurrences of icosahedral $[Cu_8S_{12}]^{16-}$ clusters in high Cu^I/M^{IV} molar ratio Cu−Ge−S[6f] or Cu−Sn−S frameworks[14c] show the stability of the cluster and its flexibility in the linkage. Thus, it can serve as building block for constructing more porous frameworks.

The compounds **1** and **2** are stable up to 400 and 360 °C, respectively. The DSC results show two endothermic phase transitions centered approximately at 400 and 525 °C for **1** and 360 and 500 °C for **2**, respectively, and TGA results show no weight loss. UV−vis reflectance spectroscopy measurements on $K_4Cu_8Ge_3S_{12}$ and $Rb_4Cu_8Ge_3S_{12}$ confirmed that they are wide-bandgap semiconductors. The optical absorption spectrum of **1** and **2** reveals the band gaps of 2.2 and 2.3 eV (Figure 4), which are consistent with the color of the compounds. These band gaps lie in the energy range suitable for visible-light photocatalytic applications.[6e] The band gaps of these two compounds have some extent of red shift compared with other Cu−Ge−S open-framework phases.[4,5b,6f] This can be partially ascribed to the contribution of more Cu^+ sites in the framework. The preliminary ion-exchange experiment of compound **1** indicated that about 84% K^+ ions can be exchanged by Na^+ ions in NaCl aqueous solution, and the framework remained intact after ion-exchange, as confirmed by powder XRD data (Figure S3 in Supporting Information). Recently, $Na_4Cu_8Ge_3S_{12}$ with the same framework has been successfully synthesized in our laboratory. Further studies on ion-exchange and ion conductivity properties are in progress.

In conclusion, two copper-rich open-framework sulfides $K_4Cu_8Ge_3S_{12}$ (**1**) and $Rb_4Cu_8Ge_3S_{12}$ (**2**) have been synthesized under solvothemal conditions, and their optical properties were investigated. In these two structures, Ge^{4+} ions were isolated and linked high symmetrical $[Cu_8S_{12}]^{16-}$ clusters to form 3D frameworks with perovskite ($CaTiO_3$) structure. Furthermore, the $[Cu_8S_{12}]^{16-}$ cluster behaving like a pseudo-octahedral atom can serve as building blocks for construction of more porous frameworks using different linkers.

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Supporting Information Available: Details for the synthesis and analytical techniques used in the present work, ion-exchange experiment details, DSC curves, XRD, and crystallographic information files (CIF) for compounds **1** and **2**. This material is available free of charge via the Internet at http://pubs.acs.org. CSD 421629 and 421628 contain the supplementary crystallographic data for **1** and **2**, respectively.