

Intermetallic Compounds with 1D Infinite Tunnels. Syntheses and Structures of AAu_4In_2 ($A = K, Rb$)

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Explorations of diverse alkali-metal–triell systems have led to the discovery of many new materials with novel structural features.¹ Inclusion of a late transition element, to gain the capability to tune both atom size and valence electron count, has been very effective in opening routes to new phases. Some unusual clusters so discovered include a fullerene-like species In_{74} in $Na_{96}In_{97}Z_2$ ($Z = Ni, Pd, Pt$),² buckyballs M_{60} ($M = Ti/Cd$) in $Na_{13}(Cd_{0.7}Ti_{0.3})_{27}$,³ and triply fused indium icosahedra resembling β -boron in $K_{34}(In/M)_{105}$ ($M = Li, Mg, Au, Zn$).⁴ Here we report the syntheses and characterizations of two intermetallic compounds AAu_4In_2 ($A = K, Rb$) in a structure in which infinite 1D tunnels are present in the Au–In framework, analogous to those of some microporous zeolites.

Comparable zeolite-like compounds, mainly oxides such as the hollandites, have been extensively studied regarding the cation arrangements in the tunnels and possible applications.⁵ To date, only a few zeolite-like intermetallic compounds with open tunnel structures have been reported, such as $NaTrSn_2$ ($Tr = In, Ga$)⁶ and $K_{0.4}Cd_2$.⁷ However, all of these are air sensitive and also have either disordered cations in the tunnels or disordered anions in the frameworks, which hinder their further structure and property studies. Both of the present AAu_4In_2 phases are inert to air and water at room temperature, and the K compound exhibits well-ordered cations in the tunnel. Each is also the first ternary compound in that corresponding system.

The title compounds were synthesized via typical high-temperature reactions.⁸ Both crystals have a distinctive copper-like luster. The structures were determined by single-crystal X-ray diffraction methods in tetragonal space group $I4/mcm$ ($Z = 4$).⁹ Figure 1a gives an overview of the KAu_4In_2 structure via a projection along c .¹³ The structure can be described as a Au–In framework of puckered eight- and four-member rings, stacked along c to form eight- and four-member tunnels. Each tunnel atom is common to one four-member and two eight-member tunnels. The larger tunnels, Figure 1b, can be viewed in terms of crownlike units $[In_{4/2}Au_4Au_4In_{4/2}]$ (dotted black lines) condensed along c . The one-dimensional voids or “octagonal” tunnels are occupied by the cations. Remarkably, the construction resembles that of zeolites in which the aluminosilicate frameworks have channels occupied by alkali-metal cations. The present structure has atoms in three crystallographic positions: A in $4a$ (422), Au in $16l$ ($.m$) and In in $8h$ ($m.2m$) sites. It can be viewed as a superstructure of $K_{0.4}Cd_2$ with a tripled c axis, but the binary has only two crystallographic positions: K ($4c$, with 36.8% occupancy) and Cd ($8h$).⁷ With a very short c axis (2.878 Å), $K_{0.4}Cd_2$ has both a small c/a ratio (0.314) and a very short distance between fractional K atoms (1.44 Å). Both of the present compounds show more reasonable cation–cation distances: K–K, 4.184 Å and Rb–Rb, 4.137 Å.

Powder patterns of both products before and after overnight soaking in water show no differences in the line intensities or positions. The refinement results on the single-crystal data collected

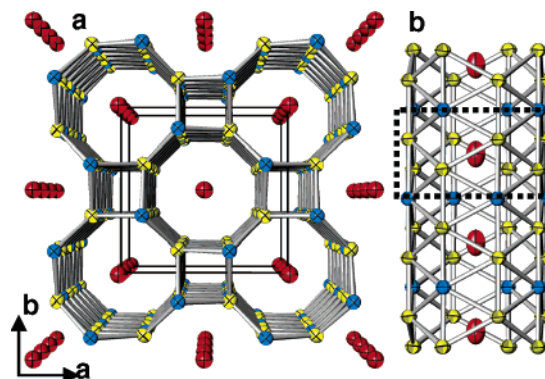


Figure 1. (a) General [001] view of KAu_4In_2 and (b) the large tunnel along c ; the crownlike repeating unit $[In_{4/2}Au_4Au_4In_{4/2}]$ is marked by dotted lines. The In, Au, and K atoms are blue, yellow, and red, respectively (85% displacement ellipsoids).

for a KAu_4In_2 crystal before and after being treated overnight with water or 12 M HCl(aq) are identical. Further X-ray photoelectron spectra and Auger experiments on a KAu_4In_2 powder sample kept in air for 2 months showed oxidation of only ~ 15 nm on the surface of the sample. Such a thin oxide film might be protective in air but not in concentrated HCl(aq). The free diameters along the tunnel may be more responsible for the stability. Such stability is also shown in some intermetallic compounds with clathrate type structures, such as $Cs_8Na_{16}Si_{136}$, $Cs_{30}Na_{2.5}Sn_{162.6}$, and Rb_8Sn_{44} , in which the cations reside inside closed cages.¹⁴ Even though the present structure displays a tunnel construction, the sizes of these particular tunnels are apparently still small enough to trap the cations. Considering the shorter unconstrained K–In distances in most intermetallic compounds,^{1,15} ~ 3.65 Å, and a K^+ crystal radius of 1.52 Å (CN = 6),¹⁶ we conclude that the indium van der Waals’ radius is about 2.13 Å. From this, the smallest free diameters along the tunnel occur at the transverse square section around indium (blue) with “free” radii of ~ 1.19 and ~ 1.28 Å for K and Rb phases, respectively. These are much smaller than the six-coordinate crystal radii of K^+ (1.52 Å) and Rb^+ (1.66 Å).¹⁶ In another view, the distances from the tunnel center to the In are 3.32 and 3.41 Å for K and Rb compounds, respectively, shorter than any respective A–In distances reported.^{1,15,17} So the cations actually appear trapped inside of the crownlike units $[In_{4/2}Au_4Au_4In_{4/2}]$. On the other hand, the air-sensitive $K_{0.4}Cd_2$ with a similar structure has a tunnel-center-to-Cd distance of 3.50 Å, even larger than that in the present Rb compound.

Another interesting feature of these compounds is the cation arrangements in the tunnels. Elongation and partial occupancy of cations in a tunnel are quite typical for tunnel-like structures with large cations, such as $K_{0.4}Cd_2$,⁷ $NaGaSn_2$,^{6a} and all hollandite-type compounds except $K_2Cr_8O_{16}$.⁵ However, KAu_4In_2 has a fully occupied and well-ordered K site with only a slightly larger displacement along the c axis,¹⁸ $u_c = 0.25$ Å vs $u_a = 0.18$ Å normal

to the tunnel (u_c and u_a are the square roots of U_{33} and U_{11} in a tetragonal system, respectively), whereas Rb shows a quite large anisotropic displacement, $u_c = 0.43 \text{ \AA}$ vs $u_a = 0.15 \text{ \AA}$ ($U_{33}/U_{11} = 9.1$). An occupancy refinement for the Rb site gives essentially the full value. Elongation of the Rb distribution is confirmed by the Fourier synthesis map. We assume the observed displacements of the cations are related to the relative sizes of cations and the tunnels. More experiments designed to mix K and Rb gave $K_xRb_{1-x}Au_4In_2$. Two structural refinements showed that K and Rb co-occupy the same position in the tunnel ($x = 0.87, 0.65$, Supporting Information). As expected, the cations show more elongation along the tunnel axis with increasing Rb content, $u_c = 0.28, 0.38 \text{ \AA}$ for $K_{0.87}Rb_{0.13}Au_4In_2$ and $K_{0.65}Rb_{0.35}Au_4In_2$, respectively, whereas the displacements normal to these are almost the same, $\sim 0.12 \text{ \AA}$. Even though these values are relatively sensitive to the qualities of the single crystals and the absorption corrections, one still can see that the larger cation displacement goes with increased Rb content. In terms of interactions between the cations and atoms in the tunnels, the greater delocalization of Rb in the tunnel is consistent with some unusual changes from the K to Rb compound: the tunnel diameter only increases $\sim 0.1 \text{ \AA}$, whereas the diameters of cations change about 0.3 \AA ,¹⁶ and the c axis becomes even shorter by 0.1 \AA . However, the interactions in both compounds are still very weak according to the following.

Linear muffin-tin-orbital calculations in the atomic sphere approximation¹⁹ for both title phases show that the Fermi levels intersect finite DOS states in both and the empirical metallic character of KAu_4In_2 is in agreement with its observed metallic property.²² (All densities-of-states (DOS) and crystal orbital Hamilton population (–COHP) data are given in the Supporting Information.) The integrated crystal overlap Hamilton populations (–ICOHP) were also determined, these being analogous to but of more significance than the Mulliken overlap populations from extended Hückel methods as measures of relative bond strengths.²⁴ The –ICOHPs for Au–In and Au–Au are almost the same in both compounds, about 1.3 and 1.2 eV/bond, respectively. The former is comparable to that of Au–In in the Na_3AuIn_2 structure with interlinked $In_4@Au_4$ tetrahedral stars.²⁵ All cation–anion –ICOHP values are quite small: K–In 0.024; K–Au 0.096; Rb–In 0.019 and Rb–Au 0.075 eV/bond, indicating their relatively weak bonding interactions. To have a hint about the relative strengths of these interactions, the –ICOHP value for Rb–Au (3.56 \AA) in $RbAu$ (CsCl type) calculated by the same method is 0.08 eV/bond, close to those in the present compounds. Band gaps at E_F for $RbAu$ from earlier band structure calculations as well as ours are consistent with photoelectron spectroscopic results.²⁶ The very weak bonding interactions make the present air and moisture insensitive compounds good candidates for further property studies.

Only a few intermetallic compounds with tunnel structures have been reported, and they are excluded from some property studies because of air sensitivity, except for KAu_4Sn_2 .¹³ Here we report a series of intermetallic compounds $K_xRb_{1-x}Au_4In_2$ ($x = 0-1$) with 1D infinite tunnel frameworks that are air and moisture inert, even in concentrated HCl(aq). More property studies on the compounds are currently under way.

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Supporting Information Available: Crystallographic data tables, a combined single-crystal X-ray crystallographic information file (CIF) for $K_xRb_{1-x}Au_4In_2$ ($x = 1, 0.87, 0.65, 0$), and plots of DOS and –COHP for both KAu_4In_2 and $RbAu_4In_2$. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (8) Once the stoichiometries had been identified by crystallography, pure phases of both compounds were synthesized from stoichiometric amounts of the elements which were sealed in tantalum containers by arc-welding under argon and enclosed in evacuated silica tubes. The samples were allowed to react at $550 \text{ }^\circ\text{C}$ for 6 h, slowly cooled ($3 \text{ }^\circ\text{C/h}$) to $350 \text{ }^\circ\text{C}$, held for 10 days, and then slowly cooled ($3 \text{ }^\circ\text{C/h}$) to room temperature.
- (9) Single-crystal diffraction data were collected at 293 K on a STOE IPDS II single-crystal X-ray diffractometer with Mo $K\alpha$ radiation with the aid of the supplied STOE software.^{10a} The data were corrected for Lorentz and polarization effects, and a numerical absorption correction was accomplished with the program X-SHAPE.^{10b} Both structures were solved by direct methods and refined with SHELXTL in space group $I4/mcm$.¹¹ The full-matrix least-squares refinement converged at $R1/wR2 = 0.0411/0.1060$ [$I > 2\sigma(I)$] and $0.0744/0.1116$ for all data with 248 reflections and 14 variables for KAu_4In_2 , and at $R1/wR2 = 0.0540/0.1299$ and $0.0832/0.1363$ (all data) with 259 reflections and 14 variables for $RbAu_4In_2$ (Supporting Information). The lattice parameters obtained via the WinXPOW program¹² from Huber 670 Guinier powder camera data are as follows: $a = b = 8.666(1), 8.830(3) \text{ \AA}$, $c = 8.368(3), 8.281(6) \text{ \AA}$, $V = 628.5(2), 645.7(2) \text{ \AA}^3$ for KAu_4In_2 and $RbAu_4In_2$, respectively.
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