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Synthesis and Structure of $K_3Mg_{20}In_{14}$, a Stuffed Variant of the $BaHg_{11}$ Structure Type with a Magnesium–Indium Network

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The phase $K_3Mg_{20}In_{14}$ was synthesized via high-temperature reactions of the elements in welded Ta tubes. The cubic crystal structure established by single-crystal X-ray diffraction means [space group $Pm\bar{3}m$, $Z = 1$, $a = 9.769(1)$ Å] features a 3D Mg–In network formed by $K@Mg_{12}In_{10}$ units plus cuboctahedral fillers, $In@Mg_{12}$. This is the first example of a well-ordered stuffed $BaHg_{11}$ structure (Pearson symbol *cP*37). On the basis of tight-binding linear muffin-tin orbital, atomic sphere approximation calculations, the electronic structure of the compound shows dominant Mg–In interactions and substantial participation of Mg in the overall network bonding. Both In–In and Mg–In bondings are effectively optimized at the Fermi level. The Fermi energy cuts through substantial densities of states, consistent with the measured metallic property.

Exploration of systems containing group 13 triel and alkali or alkaline-earth metals has uncovered an abundance of phases and highly diverse structural chemistries.[1] Extensive studies of alkali metal−triel systems, especially utilizing mixed alkali metals, have led to a remarkable variety of triel cluster frameworks, such as those in $Na_2K_{19}Tl_{21}$,[2] $K_3Na_{26}In_{48}$,[3] $Na_4K_6Tl_{13}$,[4] and KNa_3In_9.[5] The initial explorations of alkaline-earth metal−triel systems have revealed greater cation effects on the nature of the network substructures of the indides ($SrIn_4$ and Sr_3In_5).[6] Alkaline-earth metals usually act as "spacers" encapsulated within anionic networks and can therefore be treated as electron donors. Changes of the active metal atoms employed, such as their size, number, or charge, can greatly alter the structures formed and even govern the structural types of the compounds. For example, the mixing of alkali and alkaline-earth metals (or Mg) affords the capability of tuning both the cation size and valence electron count, and this appears to be effective in opening routes to new phases. A number of novel compounds have been isolated via this mixed-cation method, for example, $Li_5Ca_{18}In_{25.07}$,[7] $Na_{16}Mg_{36}Zn_{68}Al_{40}$,[8] K_2SrIn_7,[9] $(Li,Mg)_{1.63}(Zn,Al)_{3.37}$,[10] and $Na_xMg_{5-x}Ga_9$.[11] None of the group 1 or 2 elements in these compounds is a member of bonded polyhedra formed by a post-transition element, but rather they are encapsulated in these anionic networks.

Our recent research on the K−Mg−In system showed that Mg may also form part of the anionic clusters by sharing atom sites with In, such as in $K_{34}In_{91.05(9)}Mg_{13.95}$[12] and $Rb_{14}Mg_{4.5}In_{25.5}$,[13] with Mg thus behaving somewhat like Li in $K_{34}In_{92.30(7)}Li_{12.70(7)}$ and $K_{14}Na_{20}In_{91.82(8)}Li_{13.18(8)}$.[14] Continued studies in this system have led to the discovery of the first ternary compound $K_3Mg_{20}In_{14}$ with a 3D Mg−In network. Here we report its synthesis, structure, and chemical-bonding characteristics.

The title compound was synthesized via typical high-temperature reactions[15] and characterized by single-crystal X-ray diffraction methods in the cubic space group $Pm\bar{3}m$ (No. 221).[16] Figure 1a gives a general overview of the 3D Mg−In network structure, which is formed from K-centered 22-vertex polyhedra $K@Mg_{12}In_{10}$ (Figure 1b; D_{4h}). This polyhedron is elongated along the 4-fold axis and capped on opposed tetragonal faces by two In1 atoms (green). [It can also be described in terms of (distorted) hexagonal prisms

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(15) Pure $K_3Mg_{20}In_{14}$ (by powder pattern) was synthesized from stoichiometric amounts of the elements in a Ta container, which was sealed by are-welding under Ar and enclosed in an evacuated silica tube. The samples were allowed to react at 500 °C for 6 h, slowly cooled (3 °C/h) to 350 °C, held for 10 days, and then slowly cooled (3 °C/h) to room temperature. The compound has a metallic luster and is air-sensitive.

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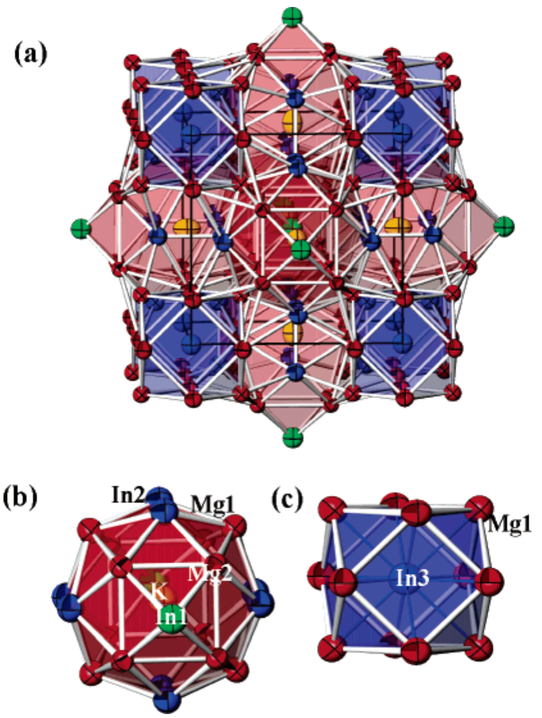

Figure 1. (a) General view of somewhat more than one unit cell of cubic $K_3Mg_{20}In_{14}$ (bond distances less than 3.5 Å are marked) with building blocks of (b) K-centered 22-vertex polyhedra $K@Mg_{12}In_{10}$ (shaded red) with point group $4/mmm$ (D_{4h}) condensed with (c) a cuboctahedral unit $In@Mg_{12}$ (blue) with point symmetry $m\bar{3}m$ (O_h).

$[(In2)_8(Mg2)_4]$ capped on the pseudo-6-fold axes (along the diagonals) by Mg1 atoms and on all side faces by additional Mg and In atoms.] Each In1 atom is shared with five other identical polyhedra, each of which lies normal to a cell face, to create the framework. The intervening sites in the framework are filled with co-condensed cuboctahedral units $In@Mg_{12}$ (blue, Figure 1c), each of which is centered by an In3 atom. The only In−In distance in the structure, 2.948 Å (In2−In2), is comparable to those found in alkali metal−In systems, such as $K_3Na_{26}In_{48}$ (2.909−3.123 Å)[3] and KNa_3In_9 (2.897−3.15 Å).[5] The Mg−Mg distances vary from 3.250 to 3.422 Å, somewhat larger than those in $Mg_2Cu_6Ga_5$ (3.00 Å)[20] and $Mg_{35}Cu_{24}Ga_{53}$ (3.16−3.32 Å),[21] probably because of the larger In atoms. The predominant Mg−In distances, 2.944−3.250 Å, are comparable to the Mg−In distance (3.057 Å) in CuMgIn,[22] the only other reported intermetallic compound with Mg−In bonds.

The $K_3Mg_{20}In_{14}$ structure is closely related to that of $BaHg_{11}$,[23] with K occupying the Ba positions and both Mg and In ordered on the four Hg positions. One difference between the two structures is the presence of an extra atom (In1), which caps a tetragonal face of the 22-vertex polyhedron (Figure 1b) and is shared by six neighboring polyhedra. This places the In1 atom in the center of a cube of Mg, $In1@(Mg2)_8$. Thus, the title compound can be described as a stuffed variant of $BaHg_{11}$ structure type. Stuffed $BaHg_{11}$ variants (Pearson symbol *cP*37) have also been found in $M_3Au_{6+x}Al_{26}Ti$ (M = Ca, Sr, Yb)[24] and $Y_3Ni_{6+x}Al_{26}Ta$.[25] However, these structures all show partial Au or Ni occupancies at stuffed 1a sites (In1) and splitting of the 12i Wyckoff sites (In2), which are occupied by mixed Au/Al or Ni/Al. The refined structures are only averages of the real structures, which were suggested having ordered supercells with doubled edges in space group $Fm\bar{3}m$.[24,25] Some expected supercell reflections were found in the X-ray powder patterns of the Ca compound.[24] The present compound shows neither any sign of disorder in the refined single-crystal structure nor any supercell reflection in its X-ray powder pattern or in the STOE single-crystal diffraction data. The refined occupancy of the In1 position is 1.005(12), and attempts failed to gain isotypic compounds with partial occupancy at this position by loading different compositions.

Another interesting feature of the title compound is the substantial role of Mg atoms in the structure. Here Mg atoms form part of the framework by occupying the later transition or post-transition element sites in the earlier structures.[24,25] Different from the recently discovered compounds $K_{34}In_{91.05(9)}Mg_{13.95}$[12] and $Rb_{14}Mg_{4.5}In_{25.5}$,[13] in which all Mg atoms are mixed with In, the present phase contains crystallographically independent Mg positions, which make it possible to study the bonding role of Mg in better detail. To gain some insight into this, first-principle electronic structure calculations were carried out on the compound by a tight-binding linear muffin-tin orbital atomic sphere approximation (TB-LMTO-ASA) method.[26] Figure 2a shows the total densities of states (DOS, black line) and partial projections for In (blue), Mg (red), and K (yellow) atoms. States that cross the Fermi level, in agreement with the observed metallic properties,[29] come mainly from In and Mg. As a matter of fact, Mg contributes almost half of the total DOS, close to that of In. Even thought there is more Mg than In in the unit cell, Mg mixing into In states is still evident, as

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(16) Single-crystal diffraction data were collected at 293 K on a STOE IPDS II single-crystal X-ray diffractometer with Mo Kα radiation with the aid of the supplied STOE software.[17a] The data were corrected for Lorentz and polarization effects, and a numerical absorption correction was accomplished with the program X-SHAPE.[17b] The lattice parameter obtained via the WinXPOW program[18] and the positions of 48 lines from a Huber 670 Guinier powder camera data is $a = 9.7696(5)$ Å and $V = 932.46(9)$ Å^3. The structure was solved by direct methods and refined with *SHELXTL*.[19] The full-matrix least-squares refinement converged at R1/wR2 [$I > 2\sigma(I)$] = 0.0267/0.0790 and R1/wR2 (all data) = 0.0322/0.0812 with 303 reflections and 17 variables (see the Supporting Information).

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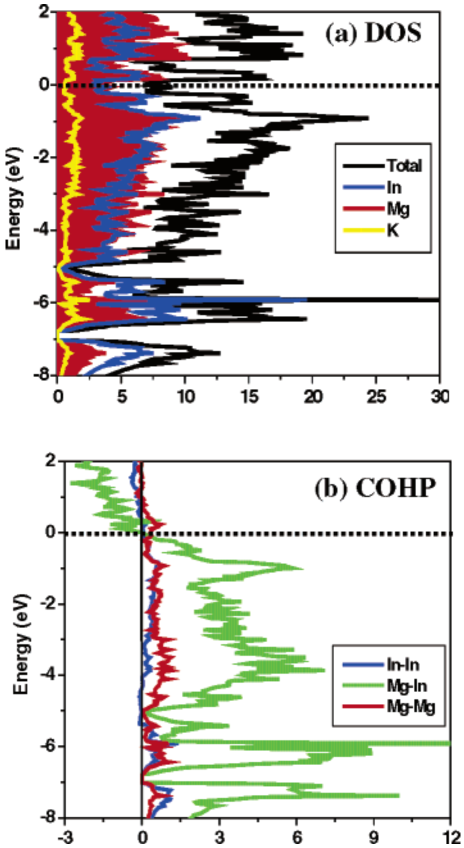

Figure 2. TB-LMTO-ASA electronic structure calculation results for $K_3Mg_{20}In_{14}$. (a) Total DOS (black) and separate partial DOS curves for In (blue), Mg (red), and K (yellow). (b) COHP curves for three different interactions: In−In (blue), Mg−In (green), and Mg−Mg (red). The dotted lines denote the Fermi level.

is strongly reflected in the fat band plots for each element (see the Supporting Information). The crystal orbital Hamilton population (COHP) results (Figure 2b) describe the relative bonding for In−In (blue), Mg−In (green), and Mg−Mg (red). At the Fermi level, both In−In and Mg−In bonds are effectively optimized, whereas Mg−Mg interactions still show small bonding character above E_F. Notice that the number of Mg−In bonds in the unit cell is more than 10 times that of In−In, which generates the very large COHP for Mg−In.

To obtain a somewhat more precise idea of the Mg involvement, extended Hückel TB (EHTB) calculations are useful because they allow Mulliken atom population analyses, which, in turn, provide insights into charge segregation within the framework. The Mulliken population analyses from EHTB[31] show that the valence electron populations of Mg1 and Mg2 are approximately 1.51e and 1.83e; i.e., their charges in this approximation are about +0.49 and +0.17, respectively. The latter values are notably smaller than those calculated in exactly the same way for Mg in Mg_2Zn_{11} (+1.49) and $Mg_2Cu_6Ga_5$ (+1.48).[20,33,34] Even considering the possible limitations of the Mulliken analyses, these values still quite clearly show that the electron transfer from Mg to In in the present phase is quite incomplete. Among these three compounds, the Mg atoms have largely different environments as to the kind and number of neighboring atoms. In the present compound, both Mg1 and Mg2 have similar neighbors: five In, six Mg, and one K for Mg1; four In, six Mg, and three K for Mg2. However, Mg in the more polar $Mg_2Cu_6Ga_5$[20] has 17 neighbors—eight Cu, eight Ga, and one Mg—and likewise in the isostructural Mg_2Zn_{11}.

Considering the LMTO and EHTB calculations, the substantial participation of Mg in the overall network in the $K_3Mg_{20}In_{14}$ is evident. On the other hand, in both Mg_2Zn_{11} and $Mg_2Cu_6Ga_5$, Mg acts more as a spacer and shows a greater electron donor character, which is also consistent with the negligible DOS contributions by Mg in band diagrams for both compounds.[20,34] The Mg atoms are not members of bonded polyhedra but rather their clear functionality is to cap faces of the polyhedra, thus often providing more polar "glue" to hold the structures together. The Mg atoms acting as spacers are also found in $Mg_2Cu_6Al_5$,[35] $Mg_{35}Cu_{24}Ga_{53}$,[21] and some Bergman phases, for example, $Na_{16}Mg_{36}Zn_{68}Al_{40}$,[8] $(Li,Mg)_{1.63}(Zn,Al)_{3.37}$,[10] and $Mg_{2-y}(Zn_xAl_{1-x})_{3+y}$,[36] in which Mg atoms exclusively occupy the more or less positively polarized sites.[10,36]

In systems involving Mg and p elements, Mg can function more as either a cation or an admix on the network positions, as in $K_{34}In_{91.05(9)}Mg_{13.95}$[12] and $Rb_{14}Mg_{4.5}In_{25.5}$.[13] Here Mg shows substantial participation in the overall bonding of the structure and forms a 3D Mg−In framework, resembling much more the Li behavior in $K_{34}In_{92.30(7)}Li_{12.70(7)}$ and $K_{14}Na_{20}In_{91.82(8)}Li_{13.18(8)}$.[14] The multifunctional roles possible for Mg allow one to obtain many different novel phases with diverse structural chemistries. Work is in progress to explore new phases with different Mg−In networks, especially for those that may contain less condensed or even isolated Mg−In clusters.

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Supporting Information Available: A figure of resistivity data and the fat band plots for each element together with CIF data for $K_3Mg_{20}In_{14}$. This material is available free of charge via the Internet at http://pubs.acs.org.

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(29) Electrical resistivities were measured by the electrodeless "Q" method with the aid of a Hewlett-Packard 4342A Q meter[30] on 88.5 mg of a powdered dispersed $K_3Mg_{20}In_{14}$ sample. The measured resistivities increase linearly over the range, and the extrapolated ρ_{298} value is about 32.5 $\mu\Omega\cdot$cm (see the Supporting Information).

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(31) Semiempirical EHTB band calculations[32a] were carried out without K on the network of $[Mg_{20}In_{14}]^{3-}$. Atomic orbital parameters were used (H_{ii} = orbital energy, eV; ξ = Slater exponent): In 5s, −12.6, 1.903; In 5p, −6.19, 1.677; Mg 3s, −9.00, 1.10; Mg 3p, −4.50, 1.10.[32b]

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