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Synthesis and characterization of $K(In_{6.5}Ag_{6.5})$

Mark S. Bailey[a], Michael A. McGuire[b], Francis J. DiSalvo[a,*]

[a]*Department of Chemistry and Chemical Biology, Cornell University, Ithaca, NY 14853, USA*
[b]*Department of Physics, Cornell University, Ithaca, NY 14853, USA*

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Abstract

The pseudo-ternary compound $K(In_{6.5}Ag_{6.5})$ has been synthesized from the elements and either excess indium or excess indium and silver. Single-crystal X-ray diffraction shows that $K(In_{6.5}Ag_{6.5})$ crystallizes in the cubic space group $Fm\bar{3}c$, $a = 13.5101(6)$ Å ($Z = 8$), and adopts the $NaZn_{13}$ structure type ($R_1 = 0.0338$). Four probe resistivity measurements show $K(In_{6.5}Ag_{6.5})$ to be a metal with a room temperature resistivity of 81 μΩ cm and a weak temperature dependence.

Keywords: Indium compounds; Silver compounds; Potassium compounds; K–Ag–In system; Flux growth; $NaZn_{13}$ structure type; Electrical resistivity; Single-crystal X-ray diffraction

1. Introduction

Silver and indium are separated by only two places in the fifth period of the periodic table. They are similar in size and electronegativity and it is therefore not surprising that a number of solid solutions exist in the binary silver–indium phase diagram [1]. Silver and indium do, however, show a divergence in their chemical reactivities; for example, indium forms at least two compounds with potassium [2] but no silver–potassium phases have been reported [1].

$NaZn_{13}$ was first reported in 1937 [3]. The structure can be viewed as a derivative of the CsCl structure type in which the zinc-centered icosahedra replace the chloride anions [4]. The $NaZn_{13}$ structure type is adopted by many combinations of the alkali or alkaline earth elements with the more electronegative group 12 atoms; for example, AZn_{13} ($A =$ Na, K, Rb, Ca, Sr and Ba) and $A'Cd_{13}$ ($A' =$ K, Rb, Cs, Sr, Ba) have been reported [5]. Beryllium, with its unusually high electronegativity for a group 2 element, is also observed to form compounds such as $CeBe_{13}$ [6].

Pseudo-ternary and ternary compounds have also been reported to crystallize in the $NaZn_{13}$ structure type. Compounds such as $Ba(Cu_{5.1}Al_{7.9})$ [7] and $Sr(Cu_9Si_4)$ [8] are formed by the replacement of the divalent atom either by a mixture of groups 11 and 13 elements or by a mixture of groups 11 and 14 elements, respectively (although $Sr(Cu_9Si_4)$ undergoes a tetragonal distortion of the cubic $NaZn_{13}$ structure type). The crystal structure of the ternary oxide $[Ag_{13}]^{4+}[OsO_6]^{4-}$ [9] can also be developed from the $NaZn_{13}$ structure by replacing the electropositive cation in $NaZn_{13}$ by the complex anion $[OsO_6]^{4-}$, and the anionic Zn_{13} icosahedra by cationic Ag_{13} icosahedra.

In the above paragraphs we have discussed the $NaZn_{13}$ structure in terms of slightly distorted, centered icosahedra. An alternative view of the structure has been suggested by Nyman and Andersson [10] who show that the $NaZn_{13}$ structure can be built from slightly distorted stellae quadrangulae. There are apparent inconsistencies with both the icosahedral and stellar quadrangular viewpoints: when the structure is drawn in terms of centered icosahedra, inter-icosahedral bonds are excluded; however, when the structure is drawn in terms of stellae quadrangulae, the radial icosahedral interactions are neglected. All the separations within the electronegative atom network are very similar and it is difficult to break the structure down in a chemically meaningful manner.

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*Corresponding author. Fax: +1 607 255 4137.
E-mail address: fjd3@cornell.edu (F.J. DiSalvo).

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The total valence electron count for the binary and pseudo-ternary compounds adopting the $NaZn_{13}$ structure type is quite uniform, which suggests that there could be an electronic driving force or magic electron count that favors certain elemental combinations and atomic ratios. Efforts have been made to decipher this driving force and, through such calculations, to suggest whether more bonding information is conveyed by drawing the structure in terms of icosahedra [7] or stellae quadrangulae [11]; however, the results of these calculations differ and it therefore appears that there is no clear theoretical support for either view. The compound $Ag_{13}OsO_6$ provides an exception to this ambiguity: atomic force microscopy suggested that crystals of $Ag_{13}OsO_6$ grow via the addition of complete Ag_{13} icosahedra from solution; within this compound, the icosahedra are not simply useful to understand the structure, rather, they are one of its chemical building blocks [12].

This paper reports the synthesis and characterisation of $K(In_{6.5}Ag_{6.5})$, a compound that crystallizes in the $NaZn_{13}$ structure type, and is the first reported phase to contain potassium, silver and indium [13].

2. Experimental

A small number of crystals of $K(In_{6.5}Ag_{6.5})$ were initially synthesized from an attempt to grow a ternary potassium–silver–nitride from an excess of molten indium: in an argon-filled glove box, 0.034 g potassium, 0.094 g of silver powder and 1 g of indium were placed into an alumina crucible. This was loaded into a 1″ OD stainless-steel tube, which was sealed with two stainless-steel end-pieces. The valves on the end-pieces were closed, the whole assembly removed from the glove box and taken to the furnace. The valves were opened to a flow of gaseous ammonia (boil-off from liquid ammonia that contains sodium to remove trace oxygen and moisture). The temperature was raised to 400 at 4 °C $(\mathrm{min})^{-1}$, where it remained for 72 h, at which point the furnace cooled to room temperature at a rate of 0.5 °C $(\mathrm{min})^{-1}$.

Following the reaction, the apparatus was returned to the glove box, where it was disassembled and the alumina crucible removed. The top of the crucible was covered with a thin layer of glass wool, inverted and placed into a fused silica tube, which was then evacuated and sealed. The silica sheathed alumina crucible was placed into a pre-heated oven at 210 °C for approximately 10 min, in order to melt the excess indium, after which the tube was quickly placed into a centrifuge and the molten indium was forced through the quartz wool, leaving the product behind.

The products of the reaction was a very small number of small ($\lesssim 50\,\mu m$) crystals, one or two of which were placed into polybutene oil for inspection under an optical microscope and for single-crystal X-ray analysis. X-ray data were collected with Mo $K\alpha$ radiation (0.71073 Å) on a Bruker SMART CCD equipped with a graphite monochromator. The Bruker software package SAINT [14] was used to integrate the data, an empirical absorption correction was applied (SADABS [15]) and the integrated data was analyzed with the SHELX97 [16] suite of programs within WinGX [17]. Following the location of all the atomic sites by direct methods, it became apparent that there was no nitrogen site in the unit cell. It was clear that a nitride had not been synthesized; rather, a pseudo-ternary intermetallic had been formed between potassium, silver and indium. Further reactions were therefore carried out.

Inside an argon-filled glove box, 0.018 g of potassium, 0.664 g of silver and 0.708 g of indium were placed into a niobium tube. These masses provided a K:Ag:In ratio of 1:13:13. Into another niobium tube was placed 0.035 g of potassium, 0.556 g of silver and 0.593 g of indium, which provided a elemental ratio of K:Ag:In::2:13:13. Both tubes were sealed under argon in a Centorr Associates Arc furnace and subsequently sealed under vacuum in fused silica tubes in order to protect the niobium from oxidation during heating.

The products of both reactions were analyzed with powder X-ray diffraction using a Scintag 2000 $\theta-\theta$ diffractometer with copper $K\alpha$ radiation. Inside an argon-filled glove box, a fraction of each sample was ground in an agate mortar and loaded onto a greased glass slide within a sample holder. The top of the sample holder was covered with Mylar and sealed with vacuum grease to prevent aerial oxidation of the sample; however, it was soon realized that the phases were inert in the laboratory atmosphere. Analysis of the powder diffraction data was carried out with the program FULLPROF [18]. No melt spinning to remove excess indium was required in either case.

The elemental composition of a number of crystals from the reaction containing a K:Ag:In ratio of 1:13:13 were analyzed by electron microprobe analysis performed with a JEOL 8900 electron microprobe. A single crystal of prismatic habit [$(0.20 \times 0.15 \times 0.56)\,mm^3$] was also selected from this sample for electrical resistivity measurements. Four gold wires (diameter 0.05 mm) were attached to the prismatic crystal with silver paste (DuPont Conductor Composition 4922N) and the resistance measured from 80 to 300 K in 2 K increments. The crystal used in the electrical resistivity measurements was not analyzed with single-crystal X-ray diffraction. However, its elemental composition was verified by electron microprobe analysis (vide infra).

3. Results and discussion

3.1. Ammonia reaction

Following the removal of the excess indium, the alumina crucible was returned to the argon-filled glove box. It was inspected under an optical microscope and found to contain only a very small number ($\lesssim 5$) of silver crystals. These were placed into polybutene oil and removed for single-crystal analysis. Several of the crystals were placed onto the goniometer head where a flow of cold nitrogen froze the oil and kept the crystals stationary. A suitable crystal was found, data was collected and the structure was solved in the space group $Fm\bar{3}c$ (number 226). Once the atomic positions were located by direct methods, it became clear that the compound adopted the $NaZn_{13}$ structure type. At this point, the program ADDSYM [17] was used in order to check for higher symmetry but none was found.

The X-ray cross-sections of silver and indium are very similar so the stoichiometry of the crystal cannot be determined from X-ray analysis alone; however, subsequent electron microprobe analysis of six other crystals (vide infra) suggested a stoichiometry $K(In_{6.5}Ag_{6.5})$; therefore, the final crystal structure refinements were performed with a 50:50 mixture of indium and silver. The atomic coordinates and displacement parameters of the silver and indium atoms occupying a given site were constrained to be identical to one another. The final crystallographic details obtained for the stoichiometry $K(In_{6.5}Ag_{6.5})$ are summarized in Table 1. The atomic coordinates found were standardized with STRUCTURE TIDY [19] and are shown in Table 2. The anisotropic displacement factors are also tabulated and presented in Table 3. Further details of the crystal structure investigation is available from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (Germany) on quoting the depository number CSD-415518, the name of the authors and citation of this paper.

Table 1
Crystal data and structure refinement details for $K(In_{6.5}Ag_{6.5})$

Empirical formula	$K(In_{6.5}Ag_{6.5})$
Formula weight (M)	1486.58
Temperature (K)	173(2)
Crystal system	Cubic
Space group	$Fm\bar{3}c$
a (Å)	13.5101(6)
Volume (Å^3)	2465.90(19)
Z	8
Density (calculated) (Mg m^{-3})	8.009
Absorption coefficient (μ) (mm^{-1})	22.251
Reflections collected	6572
Independent reflections	153 [$R_{int} = 0.0439$]
Goodness-of-fit on F^2	1.475
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0338$ $wR_2 = 0.0824$
R indices (all data)	$R_1 = 0.0344$ $wR_2 = 0.0826$

Table 2
Atomic coordinates and values of U_{eq}, the equivalent isotropic displacement parameter (Å^2 × 10^3), for $K(In_{6.5}Ag_{6.5})$

Atom	Wyckoff position	x	y	z	U_{eq}
In/Ag(1)	8b	0	0	0	16(1)
In/Ag(2)	96i	0	0.1213(1)	0.1793(1)	17(1)
K(1)	8a	0.25	0.25	0.25	14(2)

U_{eq} is defined as one-third of the trace of the orthogonalized U^{ij} tensor.

Table 3
Anisotropic displacement parameters (Å^2 × 10^3) for $K(In_{6.5}Ag_{6.5})$

Atom	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
In/Ag(1)	16(1)	16(1)	16(1)	0	0	0
In/Ag(2)	14(1)	25(1)	13(1)	9(1)	0	0
K(1)	14(2)	14(2)	14(2)	0	0	0

The anisotropic displacement factor takes the form $-2\pi^2[h^2a^{*2}U^{11} + \cdots + 2hka^*b^*U^{12}]$.

3.2. Sealed tube reactions

The two reactions performed in sealed tubes were carried out to obtain a larger quantity of the potassium–indium–silver phase for elemental analysis and transport measurements. The products of both tubes were analyzed by powder X-ray diffraction and the products of the reaction between 1K, 13In and 13Ag were analyzed first. Many peaks (~40) were observed in the powder X-ray diffractogram ($5 \leqslant {}^\circ 2\theta \leqslant 130$), seven of which could be attributed to the impurity phases $AgIn_2$ and In_4Ag_9. A face-centered cubic lattice parameter of $a = 13.5398(2)$ Å was extracted via a Le Bail refinement in space group $Fm\bar{3}c$ of the peaks not attributable to $AgIn_2$ and In_4Ag_9. This extracted lattice parameter [$a = 13.5398(2)$ Å] is, as expected, slightly larger than the lattice parameter obtained by single-crystal diffraction at lower temperatures. Although it is difficult to state from powder diffraction data alone, the diffractogram does suggest that all the potassium present in the reaction formed $K(In_{6.5}Ag_{6.5})$.

The powder X-ray diffraction pattern of the reaction between 2K, 13In and 13Ag indicated that $K(In_{6.5}Ag_{6.5})$ had also been formed, but in a reduced concentration: peaks attributable to $AgIn_2$, In_4Ag_9, KIn_4 and elemental indium were also observed.

Both samples were also inspected under an optical microscope. Larger crystals were observed to have formed from the reaction between 1K :13Ag :13In than from 2K :13Ag :13In. Furthermore, as noted above, the sample formed from 1K :13Ag :13In contained fewer impurities; therefore, this sample was used for subsequent analysis.

Silver crystals (~150 μm) of $K(In_{6.5}Ag_{6.5})$ were evident in the product mass of the tube containing a K:Ag:In ratio of 1:13:13. Eight crystals of dimension between 100 and 200 μm were taken from the sample and analyzed with an electron microprobe. Two of the eight crystals gave readings that indicated they were rich in silver and did not contain potassium. However, a total of 21 readings from smooth crystal faces of the remaining six crystals gave a mean Ag:In ratio and sample standard deviation of 1.0 ± 0.1. All the surfaces of the crystals were dotted with, presumably, excess indium and/or silver but care was taken to only analyze clean areas of the crystal faces. It is noted that the potassium K, and the silver and indium L lines are close in energy, which may lead to difficulty in fitting the peaks but, it is clear that, within experimental error, the indium and silver are present in equal amounts.

The same 21 readings as used above also yields an average Ag:K ratio and sample standard deviation of 5.7 ± 2.6. The sample standard deviation of the Ag:K ratio is much larger than that of the Ag:In ratio. This is because, with an expected K:In ratio of 1:6.5, even small variations in analysis are translated into large variations in atomic ratios. Nevertheless, the electron microprobe analysis suggests the stoichiometry used within the single-crystal X-ray refinement.

The above results also demonstrate that larger crystals of $K(In_{6.5}Ag_{6.5})$ are grown in higher yield when the reaction is performed from an excess of indium and silver. A large number of elements have some degree of solubility in molten indium at moderate temperatures [1]; hence, indium has been used a number of times as a reaction medium or reactive flux for the synthesis of intermetallic compounds, see for example [21]. It is suggested that excess indium is able to act as a reactive flux for the synthesis of $K(In_{6.5}Ag_{6.5})$.

3.3. Structure description

$K(In_{6.5}Ag_{6.5})$ adopts the $NaZn_{13}$ structure type, but with potassium occupying the sodium sites and an equal mixture of indium and silver statistically occupying the zinc sites. Such alloying of silver and indium within a pseudo-ternary compound has been observed before. For example, the family of compounds $RAg_{0.5}In_{0.5}$ (R = La [22], Pr [23], Gd–Yb [24]) have been reported, all of which crystallize either in the CsCl structure type or in a tetragonal distortion of this structure.

The structure of $K(In_{6.5}Ag_{6.5})$ can be viewed in a number of ways. One representation is shown in Fig. 1, in which there are (In/Ag)(2)-centered (In/Ag)(1) icosahedra and isolated potassium cations; indeed, this is the usual representation of compounds adopting the $NaZn_{13}$ structure type. The radial (In/Ag)(1)–(In/Ag)(2) separations are 2.925(1) Å and the surface (In/Ag)(2)–(In/Ag)(2) separations are 3.028 and 3.276 Å. However, the (In/Ag)(2)–(In/Ag)(2), inter-icosahedral separations are only 2.806 and 3.002 Å; hence, it is hard to justify the superiority of the representation shown in Fig. 1 over that shown in Fig. 2, in which all the (In/Ag)(2)–(In/Ag)(2), and none of the (In/Ag)(1)–(In/Ag)(2) distances are highlighted. From Fig. 2, it can be seen that connecting all the (In/Ag)(2) atoms leads to a three-dimensional network of stellae quadrangulae (tetra-capped tetrahedra) that forms cavities for the potassium and (In/Ag)(1) atoms. The relative merits of the connectivities shown in Figs. 1 and 2 have been discussed previously within the context of either tight binding LMTO [7] or extended Hückel calculations [11].

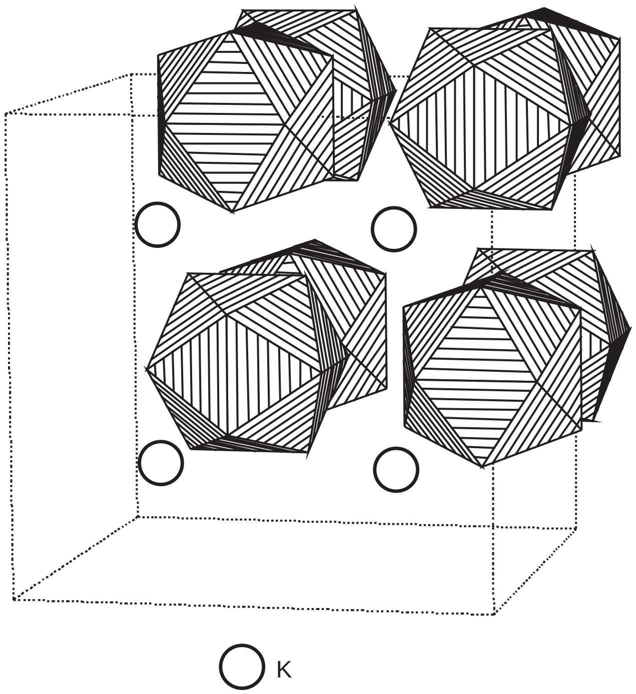

Fig. 1. The crystal structure of $K(In_{6.5}Ag_{6.5})$, in terms of In/Ag(1)-centered icosahedra.

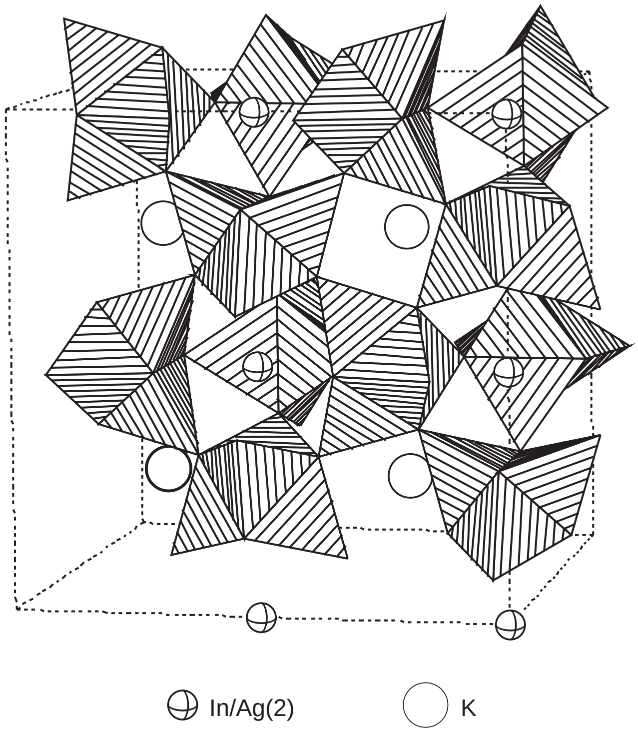

Fig. 2. The crystal structure of $K(In_{6.5}Ag_{6.5})$, in terms of In/Ag(2)–In/Ag(2) stellae quadrangulae.

It was demonstrated that in the pseudo-ternary compounds such as $BaCu_{5.10}Al_{7.90}$, the coinage metal preferentially occupies the 8b site at the center of the icosahedra [7]; however, the X-ray and electron microprobe data obtained for K($In_{6.5}Ag_{6.5}$) do not allow us to state whether silver preferentially occupies the 8*b* site in the title compound.

The coordination environments of the In/Ag(1) atoms (12 coordinate), the In/Ag(2) atoms (10-fold coordinate) and the K atoms (24 coordinate) are discussed in [5,25]. The interatomic spacings observed in K($In_{6.5}Ag_{6.5}$) are listed in Table 4. The (In/Ag)–(In/Ag) distances compare well to the closest separation in elemental indium (3.25 Å) and silver (2.89 Å) and the K–(In/Ag) separations fall within the K–In range (3.50−4.00 Å) observed in $K_{39}In_{80}$ [2].

3.4. Electrical resistivity

The measured temperature dependence of the resistivity of a single crystal of K($In_{6.5}Ag_{6.5}$) [26] is shown in Fig. 3. The resistivity increases slightly with increasing temperature from a value of 68 μΩ cm at 80 K to 81 μΩ cm at 300 K. The measured resistivity is the correct magnitude for metallic alloys such as stainless-steel (ambient temperature resistivity of stainless steel type 304 = 72 μΩ cm [27]) and is similar to 120 μΩ cm, the measured room temperature resistivity of the isostructural compound $EuCu_{6.5}Al_{6.5}$ [7].

Table 4
Selected interatomic distances in K($In_{6.5}Ag_{6.5}$)

Atoms	Number	Distance (Å)
In/Ag(1)–In/Ag(2)	12	2.925(1)
In/Ag(2)–In/Ag(1)	1	2.925(1)
In/Ag(2)–In/Ag(2)	9	2.806(1)–3.276(1)
In/Ag(2)–K	2	3.917(1)
K–In/Ag(1)	24	3.917(1)

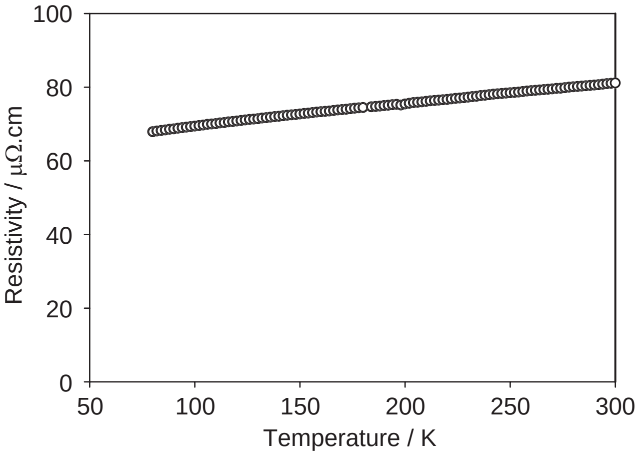

Fig. 3. The measured electrical resistivity of a single crystal of K($In_{6.5}Ag_{6.5}$).

4. Conclusion

The pseudo-ternary compound K($In_{6.5}Ag_{6.5}$) has been synthesized. It is isoelectronic with KCd_{13} and also adopts the $NaZn_{13}$ structure type. K($In_{6.5}Ag_{6.5}$) is metallic and is the first reported compound in the potassium–silver–indium ternary phase field.

Acknowledgments

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[26] No X-ray diffraction analysis of this crystal was carried out. The elemental composition was analysed with five readings from the crystal surface, yielding a Ag:In ratio of 1.05 (sample standard deviation = 0.08) and a Ag:K ratio of 4.87 (sample standard deviation = 0.81). An oxygen peak was not observed with either energy or wavelength dispersive analysis.

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