$K_2In_{12}Se_{19}$, a Complex New Structure Type Based on Icosahedral Units of Se^{2-}

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Dedicated to Prof. Dr. W. Jeitschko on the occasion of his 65th birthday

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$K_2In_{12}Se_{19}$ is a new ternary chalcogenide in the system $K_2Se–In_2Se_3$ (m.p. 997 K; colour: dark red) with the two components in a molar ratio of 1:6. This unusual solid shows a temperature-dependent order-disorder transition originating mainly from a dynamical disorder of In^{3+} at elevated temperatures. The average structure of the dynamically disordered phase at 673 K was analysed by means of high-temperature single-crystal X-ray data [$a = 1393.18(5)$ pm, $c = 1772.26(9)$ pm, $Z = 3$, $R\bar{3}$, hexagonal setting]. The most prominent feature of the complex solid is a partial structure of slightly distorted icosahedra formed by Se1 (central atom), Se3, and Se4. The topological arrangement of the icosahedra corresponds to a cubic close packing. A further independent partial structure enveloping the icosahedra is build up by Se2. The latter form large distorted polyhedra intermediate between icosahedra and cuboctahedra. In1, In2, and In3 occupy tetrahedral holes inside (In2) and outside the icosahedra (In1 and In3), whereas K is located in distorted octahedral holes. In2 and In3 are located in neighboured face-sharing tetrahedra showing an approximate 50% occupancy. They are alternatively occupied in the sense of a dynamical disorder ("average structure"). In1 and K are not affected directly by the disorder. Structural relations between $K_2In_{12}Se_{19}$ and an earlier published unusual quaternary indium chalcogenide are discussed.

Introduction

Close packing of tetrahedra based on three-dimensional interpenetrating icosahedra as structural units is common with intermetallic compounds,[1−4] but not with semiconducting or isolating solids, such as the one represented by the title compound.

We recently, however, published structural and NMR results[5,6] that surprisingly showed clear evidence for the importance of tetrahedral close packing also in the field of non-metallic solids. Typical examples are found among the group of filled β-manganese phases like $M_2Ga_6Te_{10}$ (M: Li, Na) or α-$RbAg_4I_5$,[7,8] both representing well-defined solids with interpenetrating icosahedral arrangements of the β-Mn type formed by the anions Te^{2-} and I^{1-}, respectively. A low percentage of tetrahedral holes (ca. 15%) is filled by the cations Ga^{3+} and Ag^+. Furthermore, Li^+, Na^+, or Rb^+ occupy a few additional non-tetrahedral holes ("metaprisms"). Another classical example for the importance of tetrahedral close packing with non-metals is represented by the family of filled Laves phases ("argyrodites"), in which the arrangement of anions (Se^{2-}, Te^{2-}, ...) is topologically identical to the arrangement of the Mg and Cu atoms in the cubic Laves phase $MgCu_2$.[9] Again, a low percentage (ca. 30%) of the tetrahedral holes is filled by cations.

The physical properties of filled Laves phases as well as of filled β-Mn phases are characterized by a high mobility of cations, primarily moving between face-sharing tetrahedra. Special aspects of the dynamical disorder of Ag^+ in γ-Ag_9AlSe_6 were recently analysed by means of an anharmonic structure refinement based on X-ray data.[10]

$K_2In_{12}Se_{19}$, the title compound of this paper, is a new crystalline solid that in contrast to the conventional oxidation numbers of its constituents (K^+, In^{3+}, Se^{2-}) is based on unconventional icosahedral subunits of Se^{2-}. It is evident that the structure is neither of the filled β-Mn nor of the filled Laves phase types. Furthermore, the structural characterization of the new solid is unexpectedly complicated by a temperature-dependent order-disorder transformation caused by a dynamical disorder of indium atoms and accompanied by the formation of a superstructure. The latter one is indicated by diffuse X-ray reflections and the occurrence of anti-phase domains at low temperatures. Combined X-ray and TEM (transmission electron microscopy) investigations, in particular concerning the complex microstructure of the anti-phase domains and the superstructure are currently in progress.[11] This paper is therefore mainly restricted to single-crystal X-ray results obtained for the dynamically disordered high-temperature structure (*average structure*) of $K_2In_{12}Se_{19}$ at 673 K. The ordering process at lower temperatures does not influence the general

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topology of the structure, but only specific aspects of the crystal chemical behaviour of selected In positions.

Results and Discussion

General

The title compound adds one further example to the small group of known normal and mixed valence alkali metal selenoindates that are summarized in Table 1.

Table 1. Summary of known alkali metal selenoindates

Formula	Structure type	Ref.
$LiInSe_2$	β-$NaFeO_2$	[16]
$NaInSe_2$	α-$NaFeO_2$	[17]
$KInSe_2$	$TlGaSe_2$	[18]
$RbInSe_2$	$TlGaSe_2$	[19]
$RbIn_7Se_9$	$CsIn_7S_9$	[19]
$CsIn_7Se_9$	$CsIn_7S_9$	[19]
$Rb_4In_2Se_5$	$Rb_4In_2S_5$	[18]
$Na_7In_3Se_8$	$Na_7In_3Se_8$	[20]
$Na_2In_6Se_{10}$	$Na_2In_6Se_{10}$	[21]

In most of these compounds (except the mixed valence ones) In^{3+} is exclusively tetrahedrally coordinated by Se^{2-} whereas the alkali metal atoms show larger coordination numbers with different coordination polyhedra. It turned out that the unsatisfactorily characterized mixed-valent indium chalcogenide $In_{\approx 2.01}X_3$ (X = S, Se, Te)[12] is structurally related to the title compound. A short discussion at the end of this chapter will refer to this relationship.

Selected X-ray data, positional and thermal parameters, as well as interatomic distances for the average structure of $K_2In_{12}Se_{19}$ at $T = 673$ K are summarized in Tables 2, 3, 4 and 5.

At a first glance, the overall structure looks rather complicated in that it shows up as a complex three-dimensional arrangement of corner-, edge-, and face-sharing $InSe_4$ tetrahedra with K atoms distributed in "isolated" distorted octahedra (Figure 1).

A typical feature of the average structure is the observed disorder for two (In2, In3) of the three crystallographically independent indium positions. Due to the extreme weakness of superstructure reflections for $T > 400$ K, but a continuously increasing occurrence of diffuse X-ray scattering upon cooling exclusively in layers *hkl*, with $l = 2n + 1$ (referring to the superstructure with a double *c* axis) (Figure 2) we assume a dynamical disorder at high temperatures. This disorder shows up in an approximate 50% occupancy of the respective positions (In2, In3, see Table 3). All other atomic positions (K, In1, Se) are fully occupied and do not show any irregularities.

The just mentioned diffuse scattering in the vicinity of Bragg positions in layers *hkl* with $l = 2n + 1$ indicates a successive ordering with respect to the atomic positions In2 and In3. The crystallographic aspects are seriously complicated by the ordering process and result in a *c* axis doubling and the associated formation of anti-phase domains.

Table 2. Selected X-ray data for the average structure of $K_2In_{12}Se_{19}$ at 673 K

Crystal data	
Empirical formula	$K_2In_{12}Se_{19}$
Molecular mass [$g \cdot mol^{-1}$]	2956.28
Colour	dark red
Lattice constants [pm]	$a = 1393.18(5)$ $c = 1772.26(9)$
Volume [nm^3]	29.790(2)
Z, $\rho_{calcd.}$ [$Mg \cdot m^{-3}$]	3, 4.944
Crystal system	trigonal
Space group	$R\bar{3}$ (No. 148)
Data collection	
Diffractometer	STOE IPDS, Mo-K_α, $\lambda = 71.073$ pm, oriented graphite monochromator
Crystal size [mm]	$0.25 \times 0.22 \times 0.13$
Temperature [K]	673
φ-mode	oscillation
φ-range [°], Δφ [°]	$-1 \leq \varphi \leq 360.2$, 0.6
$\theta_{min.}$ [°], θ_{max} [°]	2.85, 25.98
hkl range	$-17 \leq h \leq 17$ $-17 \leq k \leq 17$ $-21 \leq l \leq 21$
Image plate distance [mm]	70
Irradiation time/image [min]	2.2
No. of reflections, R_{int}	14538, 0.0388
No. of independent reflections	1299
Absorption coefficient [mm^{-1}]	24.446
T_{min}, T_{max}	0.0223, 0.0934
Absorption correction	numerical, crystal description with 20 faces, shape-optimised with X-SHAPE[22]
Structural analysis and refinement	
Solution method	direct methods
Refinement method	full-matrix least squares on F^2
No. of parameters	68
$F(000)$	3816
$R1$, $wR2$ [$I > 2\sigma(I)$]	0.0295, 0.0612
$R1$, $wR2$ [all reflections]	0.0346, 0.0636
Program	SHELX-97 program package[22][23]
Extinction coefficient	0.00064(3)
GooF on F^2	1.030
Largest diff. peak and hole $\Delta\rho_{max}$, $\Delta\rho_{min}$ [10^{-6} $e \cdot pm^{-3}$]	1.286, −0.959

It should be noted, however, that the ordering process does *not* remarkably change the overall structure of $K_2In_{12}Se_{19}$, which is the focus of this paper. There are, however, some important changes in detail that are closely related to the shape of the diffuse reflections, to crystal chemical aspects of the local coordination of selected atoms and the *c* axis doubling.

Table 3. Atomic coordinates, Wyckoff notations, occupancies, and equivalent isotropic displacement parameters U_{eq} [10^4 pm^2] for the average structure of $K_2In_{12}Se_{19}$ (T = 673 K)

Atom	Wyck.	x	y	z	Occ.	U_{eq}
In1	18f	0.22511(4)	0.87381(4)	0.65031(3)	0.993(4)	0.0526(2)
In2	18f	0.1187(2)	0.9207(1)	−0.56729(8)	0.453(4)	0.0641(8)
In3	18f	0.1715(1)	0.8903(1)	−0.57746(6)	0.540(4)	0.0571(6)
Se1	3b	0	0	1/2	1.001(1)	0.0657(9)
Se2	18f	0.14670(9)	0.73275(7)	0.75552(5)	0.989(5)	0.0741(4)
Se3	18f	0.19098(8)	1.03551(7)	0.69218(5)	0.998(5)	0.0599(3)
Se4	18f	0.08455(6)	0.76690(6)	0.53700(4)	1	0.0458(3)
K	6c	1/3	2/3	0.8328(4)	0.96(2)	0.141(4)

In order to gain some systematic understanding for the complex structure, the discussion of its main structural aspects is divided into three parts:

− *Primary structure:* individual coordination polyhedra

− *Secondary structure:* complex icosahedral and distorted cuboctahedral units of Se^{2-} and their decoration by In^{3+} and K^+

− *Tertiary structure:* three-dimensional connection of primary and secondary structural elements

Primary Structure

Relevant aspects of the local tetrahedral coordination of In^{3+} and the distorted octahedral ("metaprismatic") coordination of K^+ in the average structure are shown in Figure 3 (a, b). Whereas In2 and In3, located in neighbouring face-sharing tetrahedra, show an approximate 50% occupancy, the In1 position is fully occupied.

A simple distance calculation immediately demonstrates that the atomic positions In2 and In3 *cannot* be occupied *simultaneously* due to an unreasonable short interatomic distance d(In2−In3) = 103 pm. This contradiction is resolved at high temperatures by assuming a dynamic exchange process between both positions, resulting in a successive ordering at lower temperatures, a picture that is

Table 4. Anisotropic displacement parameters U_{ij} [10^4 pm^2] for the average structure of $K_2In_{12}Se_{19}$

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
In1	0.0450(3)	0.0472(3)	0.0605(4)	0.0070(2)	0.0045(2)	0.0193(3)
In2	0.064(1)	0.0510(9)	0.0467(8)	−0.0009(6)	−0.0079(7)	0.0055(7)
In3	0.0605(9)	0.0485(7)	0.0430(6)	−0.0020(4)	0.0096(5)	0.0127(6)
Se1	0.067(1)	0.067(1)	0.063(4)	0	0	0.0336(5)
Se2	0.0931(8)	0.0483(5)	0.0464(5)	0.0026(4)	−0.0029(4)	0.0095(5)
Se3	0.0755(6)	0.0611(6)	0.0524(5)	0.0025(4)	0.0072(4)	0.0411(5)
Se4	0.0395(4)	0.0462(4)	0.0489(5)	0.0031(3)	−0.0008(3)	0.0194(3)
K	0.147(4)	0.147(4)	0.129(6)	0	0	0.074(2)

Table 5. Selected interatomic distances [pm] for the average structure of $K_2In_{12}Se_{19}$

K	−Se2	344.7(3) (3×)	Se1	−In2	268.4(3) (6×)
	−Se3	350.9(5) (3×)			
			Se2	−In1	252.7(1)
In1	−Se2	252.7(1)		−In1	253.2(1)
	−Se2	253.2(1)		−K1	344.7(3)
	−Se3	263.1(1)			
	−Se4	267.75(9)	Se3	−In2	247.8(2)
				−In1	263.1(1)
In2	−Se3	247.8(2)		−In3	263.1(2)
	−Se4	261.8(2)		−In3	263.5(2)
	−Se1	268.4(3)			
	−Se4	268.6(2)	Se4	−In3	254.1(1)
				−In3	254.4(1)
In3	−Se4	254.1(1)		−In2	261.8(2)
	−Se4	254.4(1)		−In1	267.75(9)
	−Se3	263.1(2)		−In2	268.6(2)
	−Se3	263.5(2)			
In2	−In3	103.3(2)			

		Icosahedra $(Se1)_1@(Se3/Se4)_{icos.}$
Se1	−Se4	402.35(7) (6×)
	−Se3	419.62(9) (6×)
Se3	−Se3	424.5(2) (6×)
	−Se4	426.8(1) (6×)
	−Se4	434.4(1) (6×)
	−Se4	458.8(1) (6×)
Se4	−Se4	418.08(8) (6×)

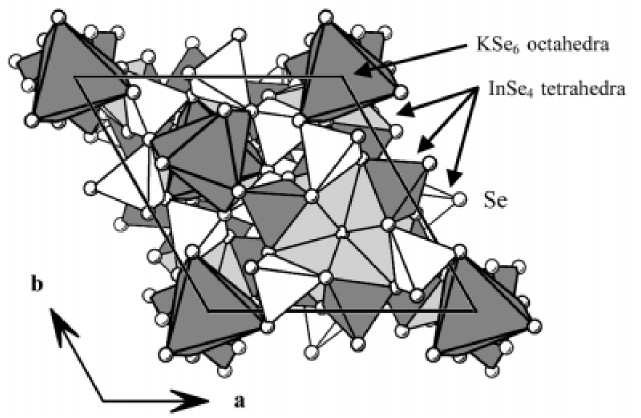
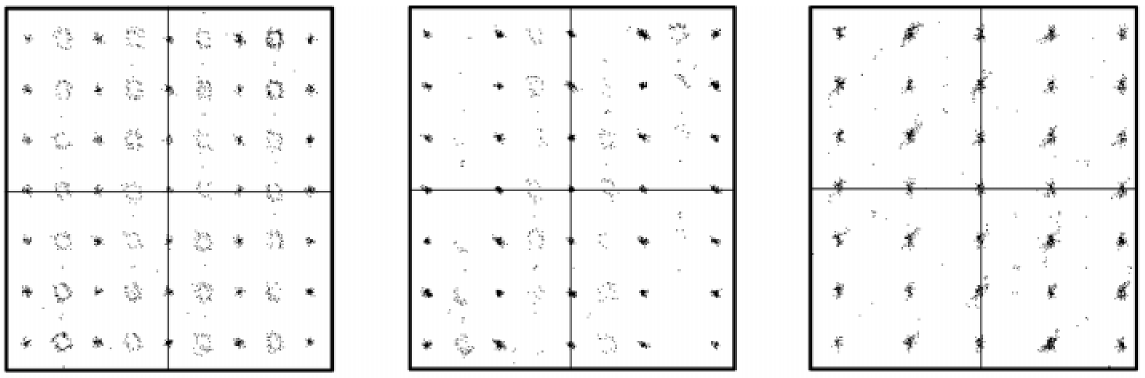


Figure 1. Projection of the average structure of $K_2In_{12}Se_{19}$ along [001] emphasising the complex arrangement of InS_4 tetrahedra and distorted KSe_6 octahedra (because of the closed polyhedra representation the In atoms inside the tetrahedra and the K atoms inside the octahedra are "invisible")



273 K 473 K 673 K

Figure 2. A temperature-dependent sequence of similar reciprocal lattice sections showing the gradual appearance of diffuse disk-shaped reflections in layers *hkl* ($l = 2n + 1$, referring to the superstructure with a double *c* axis) with decreasing temperature

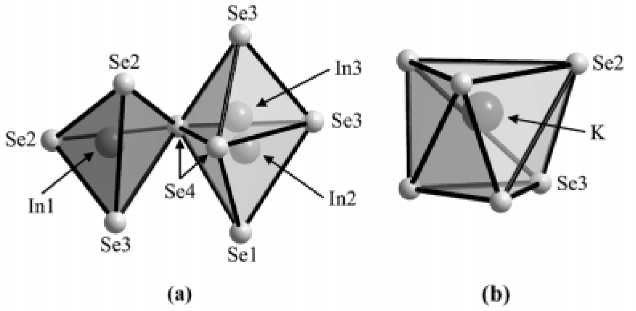


Figure 3. A comparison of the first coordination sphere polyhedra for In1, In2, In3 (a), and K (b) in the average structure of $K_2In_{12}Se_{19}$; note that In2 and In3 are not simultaneously present [$d = 103.3(2)$ pm] but represent two positions with a 50% occupancy corresponding to *one* In atom that is dynamically disordered

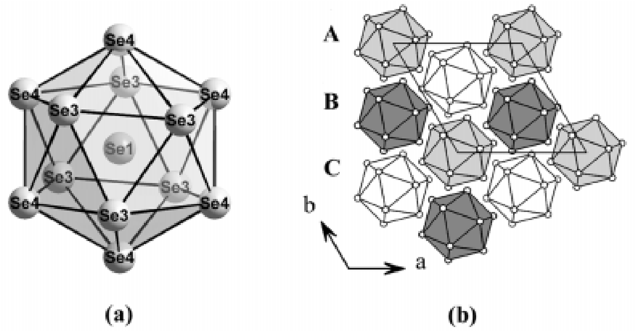


Figure 4. One icosahedral unit around Se1 formed by Se3 and Se4 (a) and a section of the three-dimensional arrangement of these units (b) representing the pattern of a cubic close packing

strongly supported by single-crystal X-ray studies at different temperatures and additional TEM investigations.

A special situation occurs for Se^{2-} for which a coordination number (CN) of 4 or 3 ($3 \times$ In $+ 1 \times$ K or $2 \times$ In $+ 1 \times$ K etc.) is usually found in similar compounds. This, however, seems to be true only in the case of Se2 and Se3 (Table 5). The seemingly unreasonable coordination numbers > 4 for Se1 and Se4 are due to the fact that both atom types are direct neighbours of the dynamically disordered In2 and In3. Obviously the type of static disorder emerging at lower temperatures is among others closely related to the attempt of the structure to reach a reasonable coordination for all Se^{2-} (CN = 3−4). Indeed, the determination of the ordered structure at low temperatures ($c_{LT} = 2 \times c_{HT}$) results in normal values for the coordination number of all Se^{2-}.[11]

Secondary Structure

Fascinating aspects of the secondary structure of $K_2In_{12}Se_{19}$ emerge upon analysing the partial structure of Se^{2-} omitting at first the In and K atoms. Figure 4 (a) shows Se1 together with Se3 and Se4 forming icosahedra of symmetry $\bar{3}$ centred by Se1. The icosahedra are made up by two types of triangles: equilateral ones formed by Se3 and non-equilateral ones formed by Se3 and Se4.

Typical interatomic distances between the central Se1 and the peripheral Se3 and Se4 are in the range of 402−420 pm. Distances between peripheral Se3 and Se4 differ somewhat more, between 418 and 459 pm (Table 5). Figure 5 (a) shows how the dynamically disordered atomic positions In2 and In3 decorate the icosahedra around Se1. As can be seen from Figure 5 (a, b), Se1 forms one apex of a tetrahedron around In2 (i.e. the central atom of the given icosahedron), whereas one apex of a tetrahedron around In3 is Se3 of a *neighbouring* icosahedron. The six In3 positions belonging to one icosahedron connect to three icosahedra *above* and to three *below* the central one, thus forming a cubic close packing of icosahedra [Figure 4 (b), Figure 5 (b)].

Figure 6 (a) shows that Se2, which does not participate in the icosahedra, forms large, strongly distorted polyhedra that encapsulate the icosahedra around Se1. They can be described as intermediate between icosahedra and cuboctahedra. The difficulties of classifying these polyhedra result from the fact that their description as cuboctahedra neglects the slight folding of the quadrilateral planes (dihedral angle: 21.5°) defined by four Se2. If one assumes the

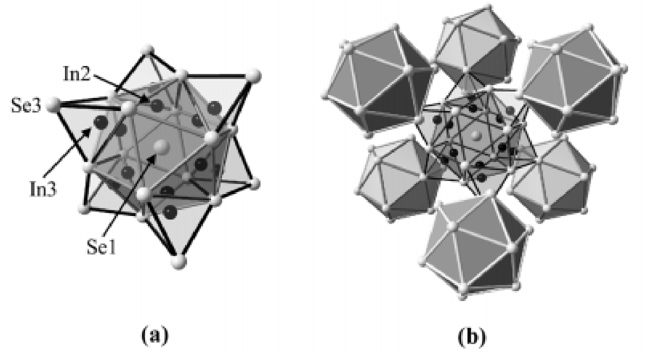


Figure 5. The decoration of the icosahedral units around Se1 by the dynamically disordered positions In2/In3 (a) and their connection to neighboured icosahedra (b)

folding line to be an additional edge, the polyhedron would better be described as an icosahedron formed by 20 strongly distorted triangular faces. Due to the just mentioned encapsulation, an endohedral unit of the type $(Se1)_1@(Se3/Se4)_{icos.}@(Se2)_{cuboct./icos.}$ can be formulated.

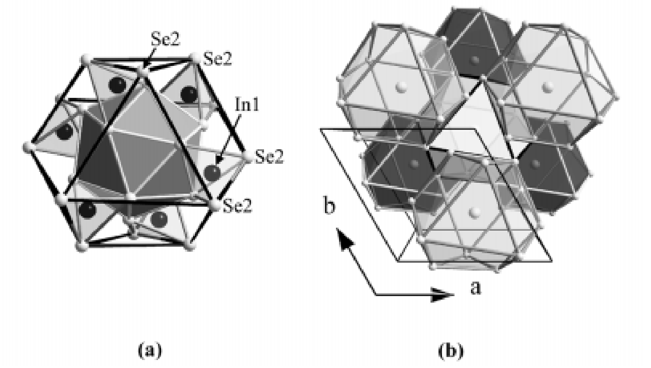


Figure 6. The large distorted cuboctahedral/icosahedral unit (see text) formed by Se2 which encapsulates the icosahedra around Se1: $Se1@(Se3,4)_{icos.}@(Se2)_{cuboct./icos.}$ and the positions of the tetrahedrally coordinated In1 in a shell between the surface of the icosahedron and the cuboctahedron/icosahedron (a); three-dimensional arrangement of the large cuboctahedra/icosahedra (b)

As Figure 6 (a) shows, atoms of the type In1 are located in tetrahedra (2 × Se2, 1 × Se3, 1 × Se4) within a shell between the surface of an icosahedron and the large surrounding cuboctahedron. The first coordination sphere of K^+ is formed by three Se3 atoms belonging to an icosahedron around Se1 and three Se2 each belonging to two *neighbouring* distorted cuboctahedra (the latter ones are not shown in Figure 7).

Tertiary Structure

As mentioned above [Figure 4 (b)], the three-dimensional arrangement of the icosahedra around Se1 corresponds to the pattern of a cubic close packing with a stacking vector parallel to [001]. Moreover, one can see from Figure 7 that the polyhedra around K are connected to somewhat smaller polyhedra along [001] that are, however, empty in $K_2In_{12}Se_{19}$. Filled and empty polyhedra form three-membered columns that connect neighbouring icosahedra along [001]. In the $In_{\approx 2.01}X_3$ phase (see below) In^{3+} is located in half of these empty polyhedra. A further consequence of the complex atomic arrangement is the fact that In2/In3 together with the icosahedra around Se1 form a three-dimensional independent substructure, which interpenetrates the arrangement of distorted cuboctahedra made up by Se2. Because Se1 atoms act as common centres also for the cuboctahedra, the topology of these endohedral units, which are connected by common edges, again corresponds to cubic-close packing [Figure 6 (b)]. Both K and In1 are cations that act as connecting links between the two partial structures.

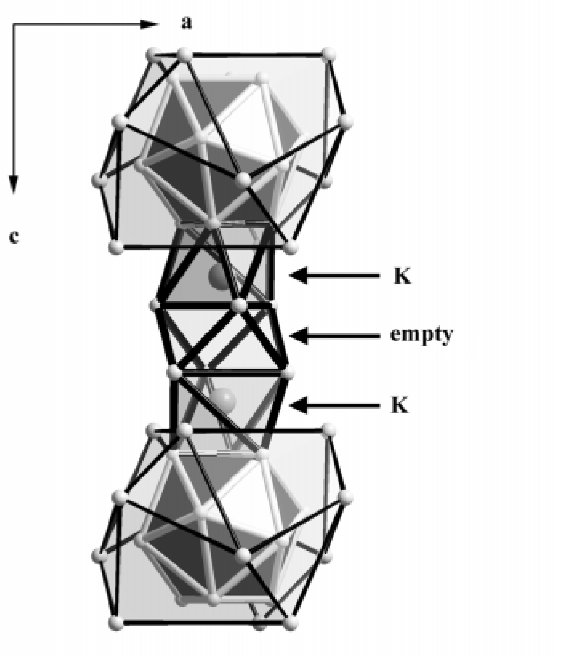


Figure 7. Section of the structure that emphasises the alternating arrangement of filled (K) and empty metaprismatic polyhedra along [001], and their connecting function between neighboured symmetrically equivalent icosahedra/distorted cuboctahedra along the same direction

Order-Disorder Transition (General Aspects)

The ordering process for In2/In3 positions at lower temperatures, which is visualised by the gradual appearance of ring shaped diffuse reflections around Bragg positions in layers *hkl* with $l = 2n + 1$ (Figure 2), and an associated doubling of the *c* axis, does not influence the above described atomic arrangement in principle (except small adjustments of the interatomic distances and angles). Face sharing between tetrahedra occupied by In atoms, however, is avoided in the ordered structure.

An important crystal chemical aspect of the ordering process is that the coordination of In2 and 3 by Se and vice versa is optimised with respect to reasonable coordination numbers for both species (see above) and with respect to interatomic distances $d(In-In)$. Due to the experimentally observed doubling of the *c* axis, the ordering patterns that do not require a *c* axis doubling can be excluded from the set of possible ordering patterns. Among the rest, there are several patterns with a non-balanced variety of short and long distances d(In−In) that can also be excluded. The remaining solution, however, leads to a structure model that inevitably produces anti-phase domains of variable size. The latter are responsible for the appearance of diffuse reflections, and reflect a complex structural frustration problem along the boundaries between adjacent anti-phase domains. Further crystallographic details of the ordered low-temperature structure, in particular with respect to results of TEM investigations, focussing on the formation of anti-phase domains are discussed in detail elsewhere.[11]

Comparison between $K_2In_{12}Se_{19}$ and the Mixed Crystal $In_{\approx 2.01}X_3$ (X = S, Se, Te)

$In_{\approx 2.01}X_3$ (X = S, Se, Te)[12] is a quaternary mixed crystal indium chalcogenide with crystallographic data closely related to those of the ordered low-temperature phase of $K_2In_{12}Se_{19}$ ($In_{\approx 2.01}X_3$: $a = 1400.3$ pm, $c = 3522.8$ pm, space group $R\bar{3}$). A closer inspection of the results published,[12] however, shows several anomalies and contradictions in particular with respect to split positions, disorder, and interatomic distances. In general, the anionic partial structure (S/Se/Te) of $In_{\approx 2.01}X_3$ and $K_2In_{12}Se_{19}$ are topologically more or less identical, although the complex secondary and tertiary structural features as described in this paper were not recognized for $In_{\approx 2.01}X_3$. In addition, there are discrepancies with respect to the positions of various cations, e.g. the positions for K atoms in $K_2In_{12}Se_{19}$ are claimed to be empty sites in $In_{\approx 2.01}X_3$. A more detailed comparison of both structures is given in ref.[13]

Conclusion

The high-temperature structure ("average structure") of $K_2In_{12}Se_{19}$ represents a new structure type for ternary selenides, which is characterized by two interpenetrating Se substructures. One is formed by Se1, Se3, and Se4, and corresponds to a cubic close packed arrangement of centred Se_{13} icosahedra. The other one consists of a three-dimensional arrangement of large distorted polyhedra (intermediate between cuboctahedra and icosahedra), and is formed by Se2 exclusively. Both polyhedra form endohedral units of the type $(Se1)_1@(Se3/Se4)_{icos.}@(Se2)_{cuboct./icos.}$ with common centre atoms (Se1). This means that the polyhedral system formed by Se2 envelopes the icosahedra. The dynamically disordered In2/In3 positions (50% occupancy) are located inside (In2) and outside (In3) the icosahedra with the tetrahedra around In3 connecting neighbouring icosahedra. The position In1 is fully occupied, and located in tetrahedra between the outer surface of the icosahedra (Se1,Se3,Se4) and the inner surface of the distorted cuboctahedra (Se2). The K atoms occupy metaprismatic holes each connecting one neighboured icosahedron and six neighboured distorted cuboctahedra.

Experimental Section

Single crystals and homogeneous powder samples of $K_2In_{12}Se_{19}$ were prepared by heating stoichiometric mixtures of the elements in evacuated dry quartz glass ampoules. The elements were heated to 1270 K for 3 h and finally quenched in ice-cold water. After homogenisation under argon, the raw product was annealed at 950 K for 14 d, resulting in a completely homogeneous product. X-ray powder diffraction data at room temp. for the lattice refinement were determined from an X-ray powder diffraction pattern (Cu-$K_{\alpha 1}$ radiation) using a Siemens D5000 X-ray powder diffractometer. For the refinement of the lattice parameters the program package WinXPow[14] was used. All lines can be indexed with a trigonal *R*-centred cell with the hexagonal constants $a = 1384.69(6)$ pm, $c = 1758.32(9)$ pm. Figure 8 shows a good agreement between the measured (293 K) and calculated X-ray powder data for $K_2In_{12}Se_{19}$ (atomic parameters based on the average structure). Superstructure reflections could not be observed because of their diffuse character and weakness.

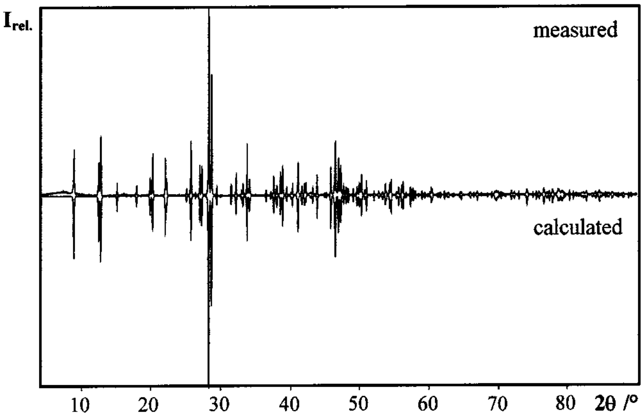


Figure 8. Comparison of experimental and calculated powder diagrams (Cu-$K_{\alpha 1}$) for $K_2In_{12}Se_{19}$ (calculation based on atomic positions for the average structure)

Well-shaped single crystals of mm size were found, both on top of the bulk product and, due to a gas-phase transport of unknown mechanism, in the colder section of the ampoule too. Powdered samples of $K_2In_{12}Se_{19}$ are reddish-brown, crystals − dependent on their thickness − dark red to black. $K_2In_{12}Se_{19}$ is not markedly air-sensitive and decomposes at 997 K. All experimental details concerning the single crystal measurement of $K_2In_{12}Se_{19}$ at 673 K are given in Table 2. The chemical composition of $K_2In_{12}Se_{19}$, especially the occurrence of K with respect to the compound $In_{\approx 2.01}X_3$, was independently proven from the X-ray results, by wavelength-dispersive analytical scanning microscopy with a CamScan microprobe CS44, equipped with a MICROSPEC WDX spectrometer. Graphics were obtained with DIAMOND 2.1.[15] Further details of the crystal-structure investigation may be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany, on quoting the depository number CSD-411816.

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