Synthesis and clathrate-type crystal structure of a solid solution in the Sn—In—P—Br system

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The solid solution of the general formula $Sn_{24-x}In_xP_{19.2+0.2x}Br_8$ ($x \le 10$) was synthesized in the Sn—In—P—Br system, and its crystal structure was determined for the composition with $x = 7.8$. This solid solution crystallizes in the cubic system, the space group $Pm\bar{3}n$, and has a type-I clathrate structure, in which the clathrate framework is composed of tin, indium, and phosphorus atoms, whereas bromine atoms occupy two types of guest positions. The unit cell parameter a increases with increasing indium content, two linear regions with different increments being observed in the $a(x)$ plot. The crystal structure of the solid solution is characterized by a complicated disorder manifested in the partial occupancy of three closely spaced positions by tin and indium atoms. The application of the Zintl formalism to the rationalization of the composition of the solid solution is discussed, and its structure is compared with the iodide analogs of similar composition but showing differences in structural details.

Key words: clathrates, solid solution, tin, indium, phosphorus, synthesis, crystal structure, Zintl phases.

Thermoelectric materials occupy a significant place among materials for new and renewable energy sources. Although thermoelectric materials are of limited use because of their insufficient efficiency, prospects of their application are estimated as great. The main areas of future application include the current generation using parasitic horsepower loss and the IR region of the solar spectrum, as well as solid-state cryogenic cooling.[1,2] An increase in the performance characteristics of thermoelectric materials, which, according to the theory, have no limitations, is a prerequisite for a wide use of these materials.[3—5] Consequently, the design of new compounds having a high thermoelectric figure-of-merit is a chemical problem.[6] This problem is complicated by the fact that the dimensionless value of the thermoelectric figure-of-merit increases with increasing efficiency of the charge carrier transport and with decreasing thermal conductivity, which is determined by the phonon transport according to the equation

$$ZT = S^2T\sigma/\kappa, \qquad (1)$$

where S is the Seebeck coefficient, σ is the electrical conductivity, κ is the thermal conductivity, and T is the absolute temperature.[5—7] Compounds combining high electrical conductivity with low thermal conductivity are scarce. According to the phonon-glass—electron-crystal (PGEC) concept, these compounds should be characterized by the spatial separation of substructures accounting for the heat and charge carrier transport.[3]

Semiconducting clathrates belong to compounds that meet the PGEC concept.[8] They comprise a specific class of inclusion compounds,[9] in which cavities in the three-dimensional lattice based on Group 14 atoms are occupied by guest atoms. Both positively charged alkali, alkaline earth metal, or europium ions and negatively charged halide or telluride ions can serve as guests.[8,10,11] In the former case, the clathrate lattice bears a negative charge, and these compounds are called anionic clathrates. In the alternative case, the positive charge is distributed over the clathrate lattice, and, consequently, these compounds are referred to as cationic clathrates. In recent years, about 40 cationic clathrates containing mainly tin as the Group 14 element were synthesized, their crystal and electronic structures were determined, and the thermoelectric properties of certain representatives of this family were investigated.[11—24] In particular, it was found that the charge carrier transport and the thermal conductivity can be independently varied by introducing various substituents into either the clathrate framework or guest positions, which is manifested in the fine structural rearrangement. For example, the maximum indium content in the Sn—In—P—I system corresponding to the formula $Sn_{10}In_{14}P_{22}I_8$ provides the formation of an ideal type-I clathrate structure (cubic space group $Pm\bar{3}n$), whereas the lower indium content ($Sn_{14}In_{10}P_{21.2}I_8$) leads to the formation of a unique superstructure with a fivefold increase in the unit cell volume due to the partial ordering of vacancies in the phosphorus sites.[14]

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In the present study, we investigated the range of the existence of the solid solution, which is formed by the partial replacement of tin by indium in $Sn_{24}P_{19.2}Br_8$,[16] in the Sn—In—P—Br system and determined fine details of its crystal structure belonging to type-I clathrates.

Results and Discussion

The results of the X-ray powder diffraction analysis of samples annealed at 550 °C in the Sn—In—P—Br system unambiguously indicate that the replacement of tin by indium in the cationic clathrate $Sn_{24}P_{19.2}Br_8$ leads to the formation of a solid solution having a type-I clathrate structure. It should be noted that the compositions of the solid solutions were chosen following the Zintl rule, according to which each framework atom tends to form an electron octet as a result of the formation of homo- and heteroatomic bonds and the lone pair localization.[25] By applying this rule to cationic clathrates,[26] it can be easily found that the theoretical limit of the replacement of tin by indium in $Sn_{24}P_{19.2}Br_8$ corresponds to the composition $Sn_{10}In_{14}P_{22}Br_8$, and the general formula of the solid solution can be written as $Sn_{24-x}In_xP_{19.2+0.2x}Br_8$. In the present study, the samples were annealed with x varying from 0 to 14 with the step $\Delta x = 2$; in some cases, the step was decreased to $\Delta x = 1$.

The formation of a phase isostructural with $Sn_{24}P_{19.2}Br_8$ was observed in the X-ray diffraction patterns for all samples with x from 2 to 12. An analysis of the X-ray diffraction patterns shows that foreing phases formed in all cases. For samples with $x \le 7$, tin phosphide Sn_4P_3 appeared to be the only impurity, whose content was not higher than 3 wt.%. For samples with $7 < x \le 10$, InP formed as the second impurity phase, the total content of impurities being estimated at 5—6 wt.%. The amount of impurities substantially increases with increasing indium content in the samples. For the sample with the maximum possible value $x = 14$, the clathrate phase was not detected. The unit cell parameter of the solid solution increases with increasing indium content in the solid solution (Fig. 1), which is consistent with the literature data[14] on the similar Sn—In—P—I system. As can be seen from Fig. 1, the plot of the unit cell parameter *versus* the indium content has three regions. The first two regions reflect different increments in the unit cell parameter with increasing x. The third region of the plot shows that the unit cell parameter remains nearly unchanged, within experimental error, for all samples with $x > 10$. This fact, along with a change in the content of impurities in the samples, indicates that the solid solution $Sn_{24-x}In_xP_{19.2+0.2x}Br_8$ exists in the composition range $0 \le x \le 9.5(5)$ at 550 °C. It is impossible to more precisely determine the concentration limits, because the impurity content in the samples cannot be accurately taken into account. It should be noted that an increase in the duration of the annealing and a change in the annealing temperature did not lead to the formation of single-phase samples. The variations in the conditions unavoidably led to an increase in the impurity content.

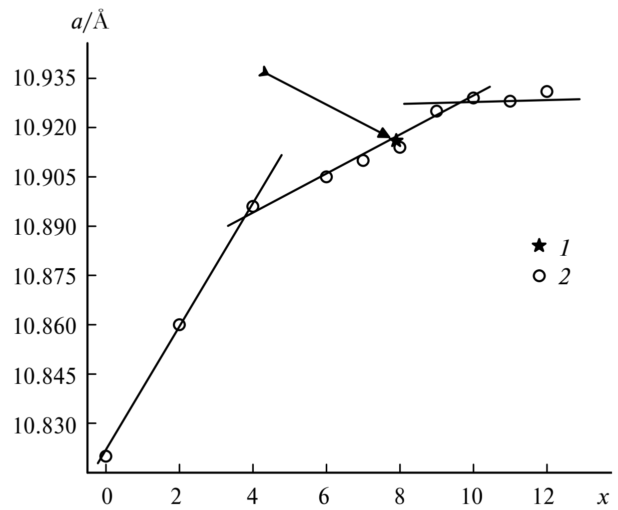

Fig. 1. Plot of the unit cell parameter a of the solid solution $Sn_{24-x}In_xP_{19.2+0.2x}Br_8$ *versus* the indium content (x): X-ray powder diffraction data (*1*) and single-crystal X-ray diffraction data (*2*) (the position is indicated by an arrow). The errors are within the symbol sizes.

The X-ray diffraction study was performed with the use of a single crystal chosen from the annealing products of the sample of the composition $Sn_{15}In_9P_{21}Br_8$, and, consequently, it would be expected that a solid solution with the indium content close to the maximum value would be formed. The determination of the symmetry and the unit cell parameters confirmed that the compound crystallizes in the space group $Pm\bar{3}n$, whereas a superstructure similar to that observed for $Sn_{14}In_{10}P_{21.2}I_8$ (see Ref. 14) is absent (Table 1).

Table 1. X-ray data collection and refinement statistics for $Sn_{15.6(9)}In_{7.9(8)}P_{21.50(3)}Br_8$

Parameter	Characteristics
Molecular formula	$Sn_{15.6(9)}In_{7.9(8)}P_{21.50(3)}Br_8$
Space group	$Pm\bar{3}n$ (№ 223)
a/Å	10.916 (1)
V/Å	1300.74(1)
Z	1
λ/Å	0.71073
d_{calc}/g cm^{-3}	5.188
μ/mm^{-1}	17.58
θ-Scanning range, deg	2.64—29.94
Total number of reflections	2189
Number of independent reflections	370
R_{int}	0.046
Number of parameters in refinement	21
R_1, wR_2 [$I > 2\sigma(I)$]	0.0396, 0.0677
Goodness-of-fit on F^2	1.285

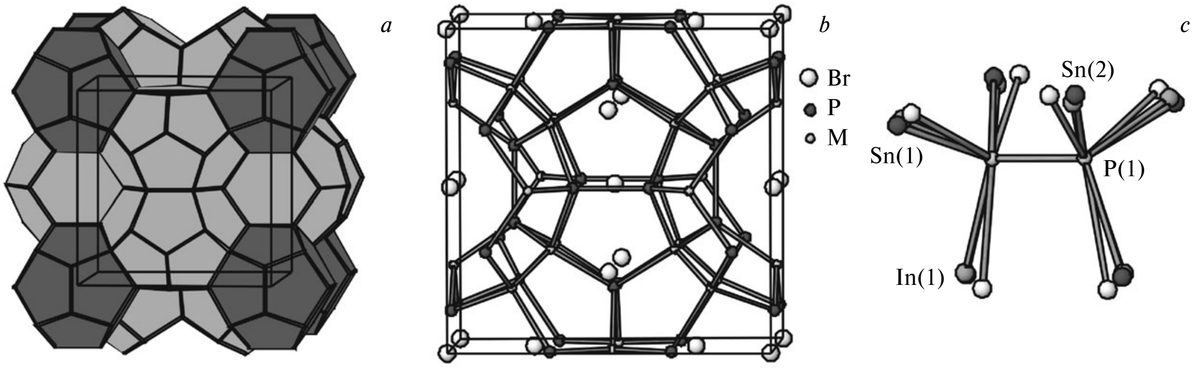

Fig. 2. Crystal structure of $Sn_{15.6(9)}In_{7.9(8)}P_{21.50(3)}Br_8$: *a*, a polyhedral representation; dodecahedra and tetrakaidecahedra are represented by dark and pale polyhedra, respectively; *b*, the arrangement of atoms in the idealized unit cell; *c*, the environment of the dumbbell consisting of P(1) atoms in the structure of $Sn_{15.6(9)}In_{7.9(8)}P_{21.50(3)}Br_8$ taking into account the disorder in the 24*k* site.

Based on the refinement of the crystal structure, the composition of the crystal was suggested as $Sn_{15.6(9)}In_{7.9(8)}P_{21.50(3)}Br_8$, which is consistent with the results of energy dispersive X-ray analysis.

The crystal structure of the solid solution under study is shown in Fig. 2. This structure belongs to type-I clathrate structures, in which tin, indium, and phosphorus atoms form a three-dimensional framework, whereas bromine atoms occupy large polyhedral cavities in the framework. The structure consists of two types of polyhedra: the smaller pentagonal dodecahedron (20 vertices) and the larger tetrakaidecahedron (24 vertices), which alternate in a ratio of 1 : 3 in such a way that there are eight polyhedra per unit cell. The bromine atoms completely occupy all positions in the centers of the polyhedra. The arrangement of the atoms involved in the clathrate framework is much more complex than that shown in Fig. 2 in the approximation of the ideal type-I clathrate structure. In the ideal structure, atoms occupy only three independent sites, 24*k*, 16*i*, and 6*c*. The structure of the solid solution under consideration is characterized primarily by the partial occupation of the 6*c* site by phosphorus atoms. In addition, the 24-fold site intended for tin and indium atoms is split into three closely spaced positions with the same multiplicity (Table 2), which are partially occupied and have different coordination. The Sn(1) and In(1) atoms are surrounded by three phosphorus atoms and are additionally bonded to the metal atom, whereas the Sn(2) atom has a different coordination. The latter atom is bonded to two phosphorus atoms (d_{Sn-P} = 2.74 Å) and four more distant metal atoms (the corresponding distances are 2.97—3.18 Å). Two independent phosphorus atoms occupying the 16- and 6-fold sites are in a typical tetrahedral coordination. The polyhedron of the P(2) atom consists of four metal atoms, whereas the P(1) atom forms three bonds with the metal atoms and one homonuclear P—P bond, whose length (2.18 Å) is typical of the single bond between two phosphorus atoms.[27]

A comparison of the crystal structure of $Sn_{15.6(9)}In_{7.9(8)}P_{21.50(3)}Br_8$ with the structures of other tin-containing cationic clathrates shows that the ternary phases $Sn_{24}P_{19.3(1)}X_8$ (X = I or Br)[12,16] can be considered as the closest analogs of the structure under consideration. In these structures, there are vacancies in the P(2) site, which do not lead to the formation of the superstructure observed in $Sn_{14}In_{10}P_{21.2}I_8$.[14] Since the atomic radii of tin and indium do not differ, the coordination of these atoms in the crystal structure is expected to be nearly the same; this contrasts with the crystal structures formed upon substitution of copper or zinc for tin in the clathrate framework.[17,18] Finally, vacancies in the structure of $Sn_{20.5}As_{22}I_8$ are formed in the tin rather than pnictogen site. This fact,

Table 2. Atomic parameters in the crystal structure of $Sn_{15.6(9)}In_{7.9(8)}P_{21.50(3)}Br_8$

Atom	*x/a*	*y/b*	*z/c*	U_{eq}/Å^2	Occupancy
Br(1)	0	0	0	0.0164(6)	1
Br(2)	1/2	1/4	0	0.0291(5)	1
Sn(1)	0.3119(3)	0	0.1186(5)	0.0133(6)	0.57(3)
Sn(2)	0.3478(10)	0	0.1518(7)	0.008(2)	0.083(5)
In(1)	0.3056(5)	0	0.1324(7)	0.0084(11)	0.33(3)
P(1)	0.19237(10)	0.19237(10)	0.19237(10)	0.0095(5)	1
P(2)	1/2	0	1/4	0.0120(8)	0.917(5)

along with the displacement of some atoms from their ideal positions, leads to the formation of a complex superstructure.[11]

The determination of the thermoelectric properties of the solid solution under consideration will be the subject of our future investigations.

Experimental

Metallic tin (99.99%), indium (99.999%), red phosphorus (97%), tin dibromide (99.5%), and bromine (99.9%) were used as the starting reagents. Red phosphorus was purified from oxygen-containing impurities by successive washing with a 30% KOH solution, twice with distilled water, twice with ethanol, and finally with diethyl ether followed by drying *in vacuo*.[16] To purify $SnBr_2$, a mixture of crushed tin dibromide and metallic tin in a weight ratio of 5 : 1 was kept in an evacuated sealed ampoule placed in a furnace at 500 °C for 48 h. After cooling, tin dibromide was separated from the tin ingot (m.p 232 °C) under a dry inert gas atmosphere.[28] The identity of all starting reagents, except for red phosphorus, was confirmed by X-ray powder diffraction analysis with a Guinier—de Wolf Nonius FR-552 camera using monochromated Cu-Kα_1 radiation.

Samples of the composition $Sn_{24-x}In_xP_{19.2+0.2x}Br_8$ (x = 0, 2, 4, 6, 7, 8, 9, 10, 11, 12, 13, and 14) were synthesized in quartz ampoules evacuated to the residual pressure of ~10^{-2} Torr. Metallic tin and indium, phosphorus, and tin dibromide were used as the starting reagents. Since $SnBr_2$ is hygroscopic, this material was handled under a dry nitrogen atmosphere. The compounds were annealed in two steps in a tube furnace. The temperatures of the first and second annealing steps and the size of quartz ampoules were varied with the aim of preparing samples with the lowest impurity content. The best results were obtained with the use of the following procedure: samples were heated to 550 °C for 10—12 h and then stored at this temperature for 5 days followed by cooling in the switched-off furnace. After cooling, the ampoules were broken in a dry box. The mixture was ground and placed in ampoules, which were evacuated, sealed, and again annealed at 550 °C for 10 days, the temperature regime being reached in 10—12 h.

X-ray diffraction analysis. The X-ray diffraction study was performed with the use of a suitable single crystal taken from the sample with $x = 9$ on a CAD-4 single-crystal diffractometer (Nonius) at ~20 °C. The unit cell parameters were refined based on 24 well-centered reflections in the angle range θ = 15—17°. The X-ray diffraction data were collected in the angle range θ = 2—30°. The correction for the Lorentz and polarization factors was performed automatically. The absorption correction was applied based on azimuthal scans of nine reflections having the χ angle close to 90°. The crystal structure was solved by direct methods using the SHELXS-97 program package,[29] which made it possible to determine the positions of two bromine atoms, two phosphorus atoms, and the metal atom. The subsequent refinement and calculations of Fourier maps showed[30] that the metal atom lies on a partially occupied 24k site, and there are two electron density peaks in the direct vicinity of this site. These peaks were ascribed also to tin atoms with partial occupancies and were included in the refinement, which resulted in the sum of the occupancies of the metal site equal to 100% within experimental error. In subsequent refinement cycles, the sum of occupancies was fixed to decrease the correlation coefficients. Since the tin and indium atoms have virtually equal scattering properties, the mixed occupancy of the metal site by these atoms was not refined, and the distribution of tin and indium over three positions was made taking into account the following considerations. One of the metal atoms has a distorted octahedral coordination described as 3+3, which is typical only of tin, and this coordination was found only for tin in all clathrates with several metal atoms.[16,17] The remaining two positions are in almost identical tetrahedral coordination with several different metal—phosphorus bond distances, but the location of indium in the less occupied site resulted in the composition $Sn_{15.6(9)}In_{7.9(8)}P_{21.50(3)}Br_8$, which is identical, within experimental error, to that determined by energy dispersive X-ray analysis (EDX, see below). The final refinement was performed with anisotropic displacement parameters for all atoms, except for tin and indium occupying closely spaced positions. The X-ray data collection and refinement statistics are given in Table 1. The atomic coordinates are listed in Table 2. Selected interatomic distances are presented in Table 3. Additional details of the crystal structure can be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany (fax: +(49)7247-808-666; e-mail: crysdata@fiz-karlsruhe.de); the deposition number CSD-424151.

Table 3. Selected interatomic distances (d) in the crystal structure of $Sn_{15.6(9)}In_{7.9(8)}P_{21.50(3)}Br_8$

Bond	d/Å	Bond	d/Å
P(1)—Sn(1)	2.600(3)	Br(1)—Sn(1)	3.642(3)
P(1)—Sn(2)	2.735(6)	Br(1)—Sn(2)	4.142(7)
P(1)—In(1)	2.523(4)	Br(1)—In(1)	3.635(4)
P(1)—P(1)	2.179(4)	Br(1)—P(1)	3.637(3)
P(2)—Sn(1)	2.505(3)	Br(2)—Sn(1)	3.653(3)
P(2)—In(1)	2.481(4)	Br(2)—Sn(2)	3.600(8)
Sn(1)—Sn(2)	2.979(11)	Br(2)—In(1)	3.747(4)
Sn(1)—In(1)	2.741(12)	Br(2)—P(1)	4.010(4)
Sn(2)—Sn(2)	3.180(18)	Br(2)—P(2)	3.859(4)
Sn(2)—In(1)	3.136(12)		

To perform EDX, a single crystal used for the determination of the crystal structure was oriented parallel to the support. The energy dispersive X-ray analysis was performed with a JEOL JSM-5510 scanning electron microscope (the accelerating voltage was 25 kV) equipped with an INCA analytical facility (Oxford Instruments). After the normalization to eight bromine atoms, the formula is $Sn_{16(1)}In_{8(2)}P_{21(1)}Br_8$.

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