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Crystal structure, thermoelectric and magnetic properties of the type-I clathrate solid solutions $Sn_{24}P_{19.3(2)}Br_xI_{8-x}$ $(0 \le x \le 8)$ and $Sn_{24}P_{19.3(2)}Cl_yI_{8-y}$ $(y \le 0.8)$

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Abstract

A solid solution of the general formula $Sn_{24}P_{19.3}Cl_yI_{8-y}$ $(y \le 0.8)$ with a crystal structure of the clathrate-I type (cubic, $Pm\bar{3}n$) was prepared by a standard ampoule technique and found to be isostructural to the previously discovered $Sn_{24}P_{19.3}Br_xI_{8-x}$ $(x = 0–8)$. The unit cell parameter linearly decreases from 10.954(1) Å for $y = 0$ to 10.933(1) Å for $y = 0.8$. $Sn_{24}P_{19.3}Cl_yI_{8-y}$ $(y \le 0.8)$ and $Sn_{24}P_{19.3}Br_xI_{8-x}$ $(x = 0–8)$ reveal a non-uniform communal distribution of the halogen atoms inside the cages of different size formed in the clathrate framework. The halogen atoms of smaller size (chlorine for $Sn_{24}P_{19.3}Cl_yI_{8-y}$ and bromine for $Sn_{24}P_{19.3}Br_xI_{8-x}$) preferentially occupy the smaller 20-vertex cages. Thereby the chlorine atoms do not show a complete segregation in the smaller cages, but mix with the iodine atoms in both types of cages. The magnetic and thermoelectric properties for $Sn_{24}P_{19.3}Cl_yI_{8-y}$ $(y \le 0.8)$ as well as for $Sn_{24}P_{19.3}Br_xI_{8-x}$ $(x = 0–8)$ were investigated. Both solid solutions are diamagnetic semiconductors as expected for Zintl phases. The core diamagnetism of the guest atoms contributes primarily to the diamagnetic susceptibility of the compounds. The band gap in the case of $Sn_{24}P_{19.3}Br_xI_{8-x}$ $(x = 0–8)$ varies from 0.03 eV to 0.14 eV and appears to be a linear function of the guest halogen atom ratios. The lowest value of thermal conductivity, 0.5 $W\,m^{-1}\,K^{-1}$ at room temperature, is observed for $Sn_{24}P_{19.3}Br_2I_6$ featuring the almost random distribution of the guest bromine and iodine atoms.

Keywords: Clathrate; Tin; Magnetic properties; Solid solution; Thermal conductivity; Zintl phase; Thermoelectric materials

1. Introduction

Clathrates belong to the large family of inclusion compounds. Their crystal structure is best described as a three-dimensional host framework trapping guest atoms or molecules in cavities of different types [1]. The structure of clathrate-I is attributed to the water hydrates of a number of gases (chlorine, sulfur dioxide, etc. [2]), but is also observed for some intermetallic compounds where the cations (guests) such as alkali, alkaline-earth metals, or europium are trapped in the anionic host framework based on four-bonded group 14 elements (Si, Ge and Sn). According to the charge of the host framework, these compounds are accepted in the literature as anionic clathrates. In recent years we have described a family of the cationic clathrates, where the host framework is positively charged and anions of halogens or tellurium serve as guests. Our recent review [3] gives a brief summary of the structure and properties of the anionic and cationic clathrates based on the group 14 elements.

Compounds with the clathrate-I structure attract much attention because of their prospective application as a base for new and advanced thermoelectric materials. A good material should possess high electrical conductivity, σ, low thermal

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conductivity, κ, and have a high thermopower, S, thus the dimensionless figure of merit $ZT = TS^2\sigma/\kappa$, becomes higher. $ZT > 1$ is considered to be the limit for materials potential for application. The formulation of the "Phonon glass-electron crystal" (PGEC) concept [4] triggered the search for new materials, in particular those with effective scattering of phonons that decrease thermal conductivity, but does not impede the transport of charge carriers. The compounds with the clathrate-I structure type reasonably comply with these requirements.

Recently, the tin phosphide iodide $Sn_{24}P_{19.3}I_8$, having the structure type of clathrate-I with a quite exceptional coordination of atoms in the host framework, was discovered [5]. By substitution of iodine with bromine the solid solution $Sn_{24}P_{19.3(2)}Br_xI_{8-x}$ with the whole compositional range ($x = 0$–8) was found to form [6]. These phases can be easily rationalized by applying an inversion of the Zintl–Klemm formalism to the clathrates [3]. Namely, four electrons are required for each tetrahedrally bonded atom and vacancy within the framework. Taking into account that a tin atom possesses four and a phosphorus atom five electrons, the idealized formulation $Sn_{24}P_{19.2}\square_{2.8}X_8$ reflects that the framework provides $19.2-2.8\times 4 = 8$ excess electrons that the guest halogen atoms consume to form the X^- anion. This shows that this clathrate is a valence compound within the accuracy of determination of its composition, $Sn_{24}P_{19.3(2)}I_8$ [5]. In this work, we report on synthesis, crystal structure, and compositional range of a new solid solution $Sn_{24}P_{19.3}Cl_yI_{8-y}$ with clathrate-I structure and the transport and magnetic properties of the particular composition $Sn_{24}P_{19.3}Cl_{0.5}I_{7.5}$. We also report thermoelectric and magnetic properties of the solid solution $Sn_{24}P_{19.3}Br_xI_{8-x}$ and discuss the relationship between structure, composition and properties of the cationic clathrates with the type-I crystal structure.

2. Experimental

2.1. Starting material

Metallic tin (Reakhim, 99.99%) was used as received. Red phosphorus (Reakhim, 97%) was purified by washing consecutively with 30% aqueous solution of KOH, water, ethanol, diethyl ether (twice) and then vacuum-dried. Tin(IV) iodide was synthesized by the reaction of the excess of tin with iodine in CCl_4 [7]. To purify tin(II) bromide (Alfa Aesar, 99.5%) from admixtures of tin(IV) compounds, tin powder and tin(II) bromide taken in the 1:3 mass ratio were annealed in an evacuated quartz ampoule at 775 K during 72 h. The target product appeared as a colorless solidified melt and was mechanically separated from the residual tin [6]. Tin(II) chloride (ChemPur, 99.99%) was purified by sublimation in vacuum. An X-ray powder diffraction analysis (Nonius FR-552 chamber, Cu $K\alpha_1$ radiation) of tin(IV) iodide, tin(II) bromide, and tin(II) chloride confirmed their single-phase character.

2.2. Sample preparation

$Sn_{24}P_{19.3}Br_xI_{8-x}$ samples with various halogen ratios ($x = 0$–8) were synthesized from the corresponding stoichiometric mixtures of tin, phosphorus, tin(IV) iodide, and tin(II) bromide were annealed in sealed silica tubes under vacuum at 725 K for 7 days, followed by regrinding and a second annealing in sealed silica tubes at 675 K for 14 days [6].

In the system Sn–P–Cl–I, a search for the clathrate phase was carried out in the whole compositional range of halogens. For this, the $Sn_{24}P_{19.3}Cl_yI_{8-y}$ samples with $y = 1$–8 were prepared using the same two-step annealing procedure as for $Sn_{24}P_{19.3}Br_xI_{8-x}$. The sample with $y = 0.5$ was synthesized in the same two-step annealing procedure, but at a slightly higher temperature of 775 K for the first annealing, chosen by the analogy with the synthesis of $Sn_{24}P_{19.3}I_8$ [5].

Single crystals with the compositions $Sn_{24.0(2)}P_{19.24(6)}Cl_{0.25(4)}I_{7.75(4)}$ and $Sn_{24.0(2)}P_{19.24(6)}Cl_{0.49(3)}I_{7.51(3)}$ suitable for X-ray structure determination were obtained by means of chemical transport reactions in a temperature gradient of 50 K (725 K → 675 K) using Hg_2Cl_2 as a transport agent and polycrystalline samples with the nominal compositions $Sn_{24}P_{19.3}Cl_2I_6$ and $Sn_{24}P_{19.3}Cl_3I_5$, respectively. A single crystal $Sn_{24.0(2)}P_{19.3(1)}Cl_{0.80(6)}I_{7.18(6)}$ was selected from the non-equilibrium reaction product of the first annealing at 725 K for 5 days of the sample with a nominal composition $Sn_{24}P_{19.3}Cl_4I_4$.

2.3. Sample characterization

All samples were characterized by means of the X-ray powder diffraction analysis (Guinier Huber G670 Image Plate Camera, or Guinier FR-552 chamber (Nonius); $CuK\alpha_1$ radiation, $\lambda = 1.54056$ Å). The unit cell parameters were obtained from least-squares fit of the Guinier pattern using LaB_6 ($a = 4.15692$ Å) or Ge ($a = 5.6576$ Å) as an internal standard utilizing the program package WinCSD [8] or original program package POWDER. To estimate the relative amount of impurity of tin phosphide Sn_4P_3 in the samples $Sn_{24}P_{19.3}Br_xI_{8-x}$ ($x = 1$–8) and $Sn_{24}P_{19.2}Cl_{0.5}I_{7.5}$, Rietveld analysis was performed using the GSAS program package [9]. Structural data for the initial model were taken from the single crystal experiments for the clathrate-I phase and from the literature [10] for Sn_4P_3. In no case the amount of the impurity was higher than 1 mass %.

To confirm the composition of the prepared samples the EDXS analysis was performed. The surface of the pills prepared by SPS was polished by standard methods and examined in partly polarized light (ZEISS Axioplan2 optical microscope) using differential interference contrast. The elemental analysis was performed using the Philips XL30 scanning electron microscope. The analysis confirmed that the halogen ratio in the samples $Sn_{24}P_{19.3}Br_xI_{8-x}$ ($x = 2$, 3, 5 and 7) corresponds, within the 2σ limit, to the nominal composition. In the case of $Sn_{24}P_{19.2}Cl_{0.5}I_{7.5}$ the Sn/P/I ratio, normalized to 24 tin atoms, was found to be 24(1):19(1):7(1), while the chlorine content was determined only qualitatively due to the low chlorine concentration.

2.4. Single crystal X-ray diffraction experiments and structure determination

Single crystals of the three compositions (above) were mounted on a goniometer head of a CAD-4 (Nonius)