Available online at www.sciencedirect.com

ScienceDirect

Journal of Solid State Chemistry 179 (2006) 3756–3762

JOURNAL OF SOLID STATE CHEMISTRY

www.elsevier.com/locate/jssc

A facile high-yield solvothermal route to tin phosphide Sn_4P_3

Kirill A. Kovnir[a,*], Yury V. Kolen'ko[a,b], Sugata Ray[b], Jinwang Li[b], Tomoaki Watanabe[b],
Mitsuru Itoh[b], Masahiro Yoshimura[b], Andrei V. Shevelkov[c]

[a]*Department of Materials Science, Moscow State University, 119992 Moscow, Russia*
[b]*Materials and Structures Laboratory, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 226-8503, Japan*
[c]*Inorganic Synthesis Laboratory, Department of Chemistry, Moscow State University, 119992 Moscow, Russia*

Received 20 June 2006; received in revised form 8 August 2006; accepted 12 August 2006
Available online 17 August 2006

Abstract

An effective method of synthesis of tin phosphide Sn_4P_3 starting from metallic tin and amorphous red phosphorus by a low-temperature (200 °C) solvothermal reaction in ethylenediamine is offered. The key parameters of this process – duration, temperature, and the ratio of initial components (Sn/P) are studied. The structure, phase composition, and morphology of the products are investigated using powder X-ray diffraction and scanning electron microscopy. Different synthetic ways for tin phosphide are discussed and compared with the proposed one. The mechanism of solvothermal preparation of tin phosphide in ethylenediamine is discussed. It is shown that the proposed solvothermal method opens up the possibility of preparing other metal-rich phosphides.

Keywords: Tin; Phosphorus; Tin phosphide; Sn_4P_3; Solvothermal synthesis; Magnetic properties; Reaction mechanism

1. Introduction

Metal phosphides show a great variety of compositions, crystal structures, and properties. Nowadays, they have become a key constituent class of compounds for exploring new functional materials. Generally, initial material studies focused on the so-called III–V phosphides such as GaP and InP; the area of semiconducting electronics demanded the exploration of the synthesis, structural and physical properties of these compounds. Recently, other metal phosphides have found interesting applications in the field of anode materials [1] and catalysis [2] and thus have stimulated works to explore *d*-metals (Mo, W, Fe, Co, Ni, Cu) [1a-1e,2a-2j] as well as *p*-metals (Zn, Sn) [1f-1i,2k-2l] phosphides. The development of new and simple routes for the preparation of the phosphides is one of the important steps on the way to new materials.

In the review [3] *von Schnering and Hönle* had summarized all ways of preparation of the metal phosphides known by the end of the 80th. The methods include different kinds of ampoule techniques, arc melting, high-pressure techniques, thermal decomposition of higher phosphides, chemical transport reaction, synthesis in liquid ammonia, reduction of phosphates, molecular beam epitaxy, and electrolysis of phosphates. Later, *Buhro* has extended this list by reviewing metallo-organic routes to metal phosphides [4]. Most of the approaches demand high-temperature conditions and/or special devices or require operations with toxic/high-sensitive precursors; therefore, the development of convenient and effective routes for the fabrication of phosphides remains challenging. Recent advances in this area have demonstrated that some "soft chemistry" approaches can be successfully applied for phosphides preparation, where solvothermal/hydrothermal route is one of most promising and convenient ways [see 5 and references therein].

Tin phosphide Sn_4P_3 has a layered crystal structure (Fig. 1). The alternating layers of phosphorus and tin atoms are grouped into blocks seven layers thick, which propagate along the *c*-axis. All phosphorus atoms are octahedrally coordinated by tin atoms. Half of tin atoms are octahedrally coordinated by phosphorus atoms, while

---

[*] Corresponding author. Present address: Max Planck Institute for Chemical Physics of Solids, Nöthnitzer str. 40, 01187 Dresden, Germany. Fax: +49(0)351 4646 4002.
E-mail address: kovnir@cpfs.mpg.de (K.A. Kovnir).

0022-4596/$ - see front matter © 2006 Elsevier Inc. All rights reserved.
doi:10.1016/j.jssc.2006.08.012

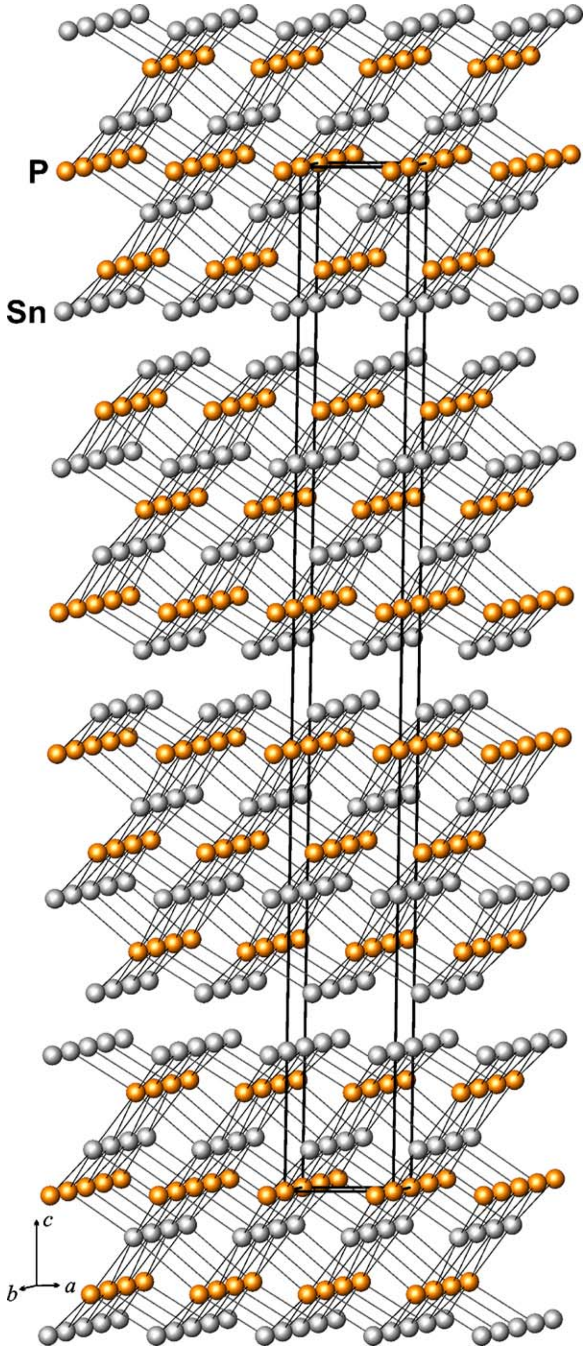

Fig. 1. A general view of the crystal structure of layered tin phosphide Sn_4P_3 (hexagonal, $R\bar{3}m$, $a = 3.9677$ Å, $c = 35.331$ Å) [6a]. Tin atoms, gray spheres; phosphorus atoms, orange spheres.

tin atoms confining each block have a 3 + 3 coordination composed by three phosphorus atoms and three rather distant (3.2 Å) tin atoms from the adjacent block. The question of oxidation numbers for the atoms in this compound is open, but one can expect the possibility of intercalation of cations in between two weakly bound tin layers. Owing to the mentioned reason, Sn_4P_3 provides an interesting material for lithium batteries [1g-1i] and is also able to catalyze reactions of the silanes alkylation [2k,2l]. According to the literature, several approaches have been realized for the synthesis of the title compound, namely: (i) the direct synthesis from tin and red phosphorus in evacuated silica tubes at the relatively high temperatures ($>550\,^{\circ}C$) [6]; (ii) the chemical vapor deposition of Sn_4P_3 films [7]; (iii) the mechanochemical synthesis [1g-1i]; and (iv) the solvothermal synthesis in nonaqueous solvents [8]. It should be emphasized, that the latter synthetic procedure is the most convenient one, but the described solvothermal routes require operations with hazardous/highly sensitive reagents such as yellow phosphorus and potassium borohydride KBH_4 [8a], or metallic sodium and sodium phosphide Na_3P [8b], which significantly limit the advantages of the solvothermal synthesis.

In this work we demonstrate the high-yield synthesis of the high-quality Sn_4P_3 by a new and facile solvothermal route from conventional reagents, metallic tin and amorphous red phosphorus powders. The mechanism of the phosphides formation during solvothermal synthesis is also discussed.

2. Experimental

2.1. Materials

Amorphous red phosphorus powder (98.0% Wako), tin metal powder (99.5% Wako), and ethylenediamine (1,2-diaminoethane) (99.0% Wako) were used as received.

2.2. Solvothermal syntheses

Appropriate amounts (Table 1) of red phosphorus and tin were mixed with 30 cm^3 of ethylenediamine in a polytetrafluoroethylene (PTFE) vessel (volume – 40 cm^3),

Table 1
Summary of the selected solvothermal reactions in 30 cm^3 of ethylenediamine starting from 5 mmol of metallic tin powder and appropriate amounts of red phosphorus

Reference	Ratio Sn/P	Synthesis condition	Phase composition
TP-1	4/3.1	160 °C, 10 h	$Sn + Sn_4P_3$[a]
TP-2	4/3.1	200 °C, 40 h	$Sn_4P_3 + Sn$
TP-3	4/6	200 °C, 40 h	$Sn_4P_3 + Sn$[a]
TP-3w	4/6	200 °C, 40 h[b]	Sn_4P_3
TP-4	4/6	200 °C, 10 h	$Sn_4P_3 + Sn$
TP-5	4/6	200 °C, 70 h	$Sn_4P_3 + Sn$[a]
TP-6	4/6.75	200 °C, 40 h	$Sn_4P_3 + Sn$[a]
TP-6w	4/6.75	200 °C, 40 h[b]	Sn_4P_3
TP-7	4/7.5	200 °C, 40 h	$Sn_4P_3 + Sn$[a] $+ X$[c]
TP-8	4/9	200 °C, 40 h	$Sn_4P_3 + Sn$[a] $+ X$[c]
TP-9	4/15	200 °C, 40 h	$Sn_4P_3 + X$[c]
TP-10	4/6	300 °C, 85 h	$Sn + Sn_4P_3$[a]

[a] Minor amount of the phase.

[b] After solvothermal synthesis the sample was washed with diluted HCl (0.1 mol/L) for 12 h.

[c] According to X-ray diffraction several additional peaks at low 2θ angles are present on the powder pattern, which cannot be attributed to any known modification of phosphorus, tin or their phosphides/oxides (supporting information, Figure S1).

the vessel was then capped by a PTFE cover and placed inside a stainless steel bomb. The bomb was sealed and kept at 160 or 200 °C for 10, 40 or 70 h. One additional synthesis was performed in a high-pressure cell made up of Hastelloy alloy at 300 °C for 85 h.

The product of the solvothermal process was collected by filtration, washed four times with distilled water and once with ethanol, and then dried at 60 °C in air. To remove the admixture of metallic tin from the as-produced samples, a washing of product was carried under vigorous stirring in 0.1 mol/L HCl aqueous solution for 12 h.

Throughout this work, a set of acronyms is used (Table 1). The first two letters mean the desired **T**in **P**hosphide (**TP**), the number of the sample follows; the last letter indicates (if applicable) the applied further processing: **w** – washing in diluted HCl.

2.3. Characterization

The grinded crystalline products were characterized by powder X-ray diffraction (XRD) using a Rigaku RINT 2000 diffractometer with Ni-filtered Cu*K*α radiation ($\lambda = 1.54178$ Å), operating at 200 mA and 50 kV. Data were collected in the 2θ range of 5–90°, with a scan speed of 0.5 °/min, and a step width of 0.02°. The unit cell parameters were refined by least-square fits of diffraction peak positions of the main phase in the hexagonal system using LaB_6 as an internal standard ($a = 4.15692$ Å) with WinCSD software [9a]. The profile refinement was carried out by Jana2000 software [9b], the summary of the results is presented in Supporting information. The morphology was studied by scanning electron microscopy (SEM) using a Hitachi S-4500 microscope operating at 15 kV. The magnetic susceptibility (χ) for the samples was measured in the external magnetic fields of 0.01, 0.1, 2.5, and 5 T over a temperature range of 2–400 K using an SQUID magnetometer (MPMS5S, Quantum Design). Samples for magnetization were prepared by placing a small amount of the sample in an AGC1 Gelatin capsule. The diamagnetic contribution from the gel cap was measured for each of the applied fields and subsequently subtracted from the sample measurements.

3. Results and discussion

The summary of selected solvothermal syntheses in ethylenediamine is given in Table 1. All our attempts to use other solvents failed. Using ethyleneglycol as a solvent led to low yields of the desired product, while the syntheses in water resulted in the formation of the tin hydrophosphate $SnHPO_3$. All discussion below is devoted only to the syntheses in ethylenediamine.

Analysis of the obtained data reveals that important parameters for the synthesis of Sn_4P_3 by solvothermal method are duration, temperature, and the initial components ratio. The powder XRD analysis of the sample **TP-1** shows that the reaction between tin and red phosphorus does not result in the formation of significant amount of Sn_4P_3 at low temperature (160 °C) and short synthetic time (10 h). The sample is mostly consisting of metallic tin with a minor admixture of the title compound.

Increasing of the reaction temperature leads to significantly higher yields of Sn_4P_3. When the stoichiometric amounts of the tin and red phosphorus are introduced into the reaction the remarkable amount of metallic tin remains unreacted. For example, for the sample **TP-2** the rough estimation from the profile refinement results in 25 wt% of metallic tin and 75 wt% of Sn_4P_3. The syntheses started from a 2 or 2.25 times excess of red phosphorus lead to practically single phase samples with small admixtures of metallic tin, samples **TP-3** and **TP-6**. Fig. 2 shows the result of the Rietveld refinement of the two-phase sample **TP-3**, from which it is estimated that the total amount of the tin admixture is ~1 wt%. For the sample **TP-6** this is even lower, being close to the detection limit of the XRD Rietveld analysis. Further decreasing of the Sn/P ratio (samples **TP-7**, **TP-8**, and **TP-9**), i.e. increasing the phosphorus excess up to 5 times, leads to diminishing of tin admixtures in the samples, but simultaneously the samples become contaminated with an unidentified phase, which diffracts poorly. The requirement of phosphorus excess during the solvothermal synthesis of copper phosphide was mentioned by Brock et al. [10]. Apparently, some equilibrium is achieved in the system between the metal, dissolved phosphorus and metal phosphide, and excess of phosphorus shifts this equilibrium towards the formation of the metal phosphide. If the solution after the solvothermal synthesis was stored in air for several days, the formation of the amorphous precipitate was observed, which was probably phosphorus.

No homogeneity range was detected for Sn_4P_3, which is inconsistent with the earlier reported wide homogeneity range [6b]. The refined unit cell parameters of Sn_4P_3 for all synthesized samples (least-squares refinement of the peak positions using the external standard) did not differ from one another within 3 e.s.d.; moreover, no systematic changes of the unit cell parameters with increasing phosphorus excess in the initial mixture were detected. For the most pure sample **TP-6w** the refinement of the unit cell parameters gives the following values (Sp. Gr. $R\bar{3}m$): $a = 3.96813(8)$ Å, $c = 35.3426(9)$ Å. The obtained values are in agreement with those reported for the bulk powder sample of Sn_4P_3: $a = 3.9677(3)$ Å, $c = 35.331(4)$ Å [6a], but differ from the unit cell parameters reported for the Sn_4P_3 nanopowder: $a = 3.9701$ Å, $c = 35.012$ Å [8a].

The influence of the duration of the synthesis on the nature of the product was also investigated. Three syntheses with the constant Sn/P ratio (4:6) but different reaction time were performed at 200 °C. For the sample **TP-4** (duration 10 h) ~30 wt% of metallic tin was found in the product, while for the sample **TP-3** (duration 40 h) only ~1 wt% of metallic tin was found. Further increase of the duration of the synthesis (sample **TP-5**, 70 h) leads to

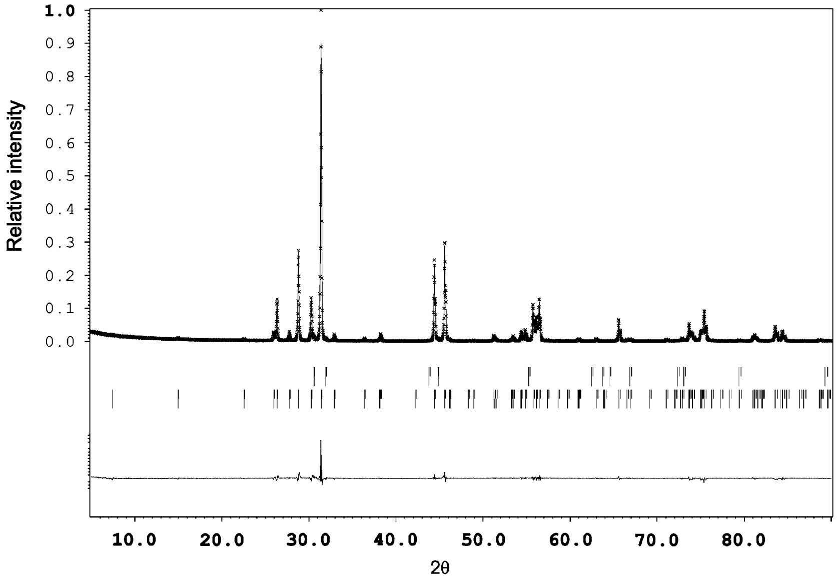

Fig. 2. Rietveld analysis of the X-ray diffraction pattern of the sample **TP-3**. Experimental data points are shown as dots and theoretical fits are shown as solid curves. Tick marks below the fit correspond to the positions of the Bragg reflections expected for the β-tin (upper row) and tin phosphide Sn_4P_3 (lower row) structures. The curve at the bottom represents the difference between the observed and calculated patterns.

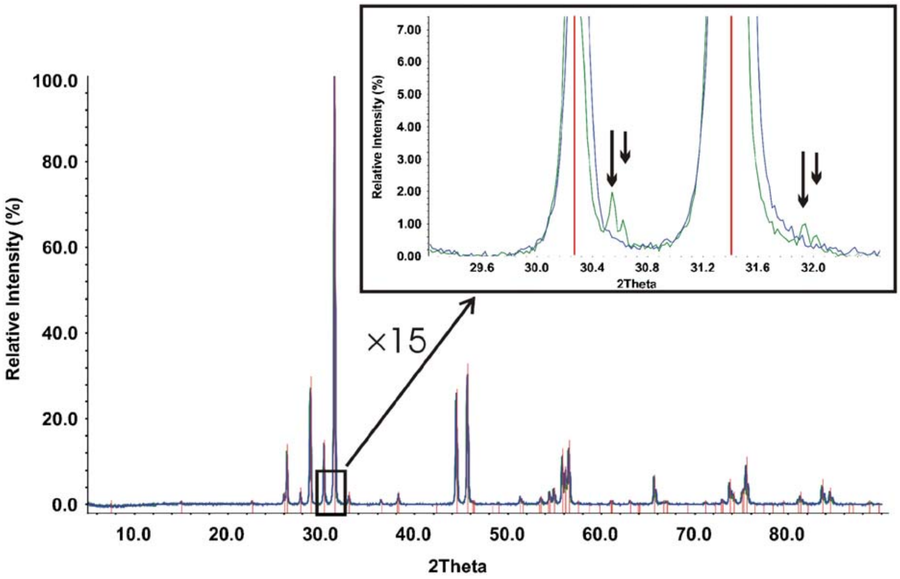

Fig. 3. Comparison of the powder diffraction pattern for the samples **TP-3** and **TP-3w**, green and blue lines, respectively. An inset shows the enlarged region from 29.2° to 32.4° 2θ, where two most intensive peaks of β-tin are expected. The positions of the Sn_4P_3 diffraction peaks are shown by red vertical lines, while the tin diffraction peaks are marked with black arrows.

further reduction in tin content, although a complete removal of the tin admixture could not be achieved even in this case.

The most pure samples were synthesized at 200 °C starting from the tin/phosphorus ratio 4:6 or 4:6.75. The minor tin admixture (less than 1 wt%) in these samples can be easily removed by washing with diluted hydrochloric acid, thus the phase pure samples of Sn_4P_3 can be obtained as demonstrated for the sample **TP-3w** (Fig. 3, inset). The Sn_4P_3 phase is not affected by acid washing, it preserves its crystallinity as revealed by XRD (Fig. 3).

The morphology of a solvothermally produced polycrystalline Sn_4P_3 observed by SEM is shown in Fig. 4A. The sample **TP-3** consists of relatively big aggregates without any texturing, the particles size ranges from several hundred nanometers to a few micrometers. In addition, the presence of trace amounts of a raw metallic tin was detected by SEM in the **TP-3** sample (Fig. 4A, inset), which is in agreement with the XRD data. The morphology of the initial tin metal powder is shown in Fig. 4C. Washing of the **TP-3** sample with diluted HCl does not lead to significant changes in the microstructure (Fig. 4B), but at the same

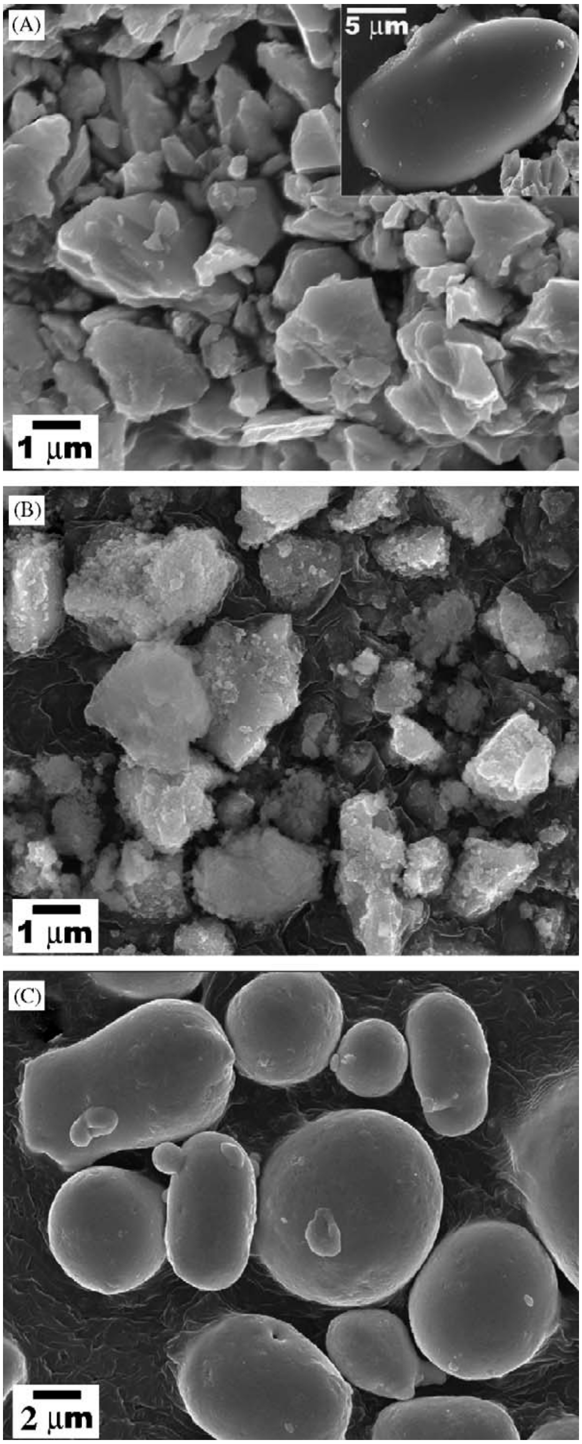

Fig. 4. SEM microphotographs are shown for (A) a solvothermally prepared polycrystalline Sn_4P_3 with the inset illustrating an observed trace of the metallic tin (sample **TP-3**); (B) a view of the morphology of the same sample after washing in diluted HCl (sample **TP-3w**); (C) a typical morphology of the initial tin metal powder.

time a slight decreasing of the average size of the aggregates was observed. That may be related to a milling-like effect during the 12 h vigorous stirring of the small amount of a powder in a relatively large volume of the aqueous solution, but seems not to be caused by the acidic treatment. It should be noted that no admixture of tin metal was detected by SEM for the washed **TP-3w** sample.

Preliminary investigations of the magnetic properties of synthesized samples (**TP-3w** and **TP-6w**) reveal a diamagnetic behavior of the Sn_4P_3 compound. It should be noted that low field measurements (0.1 and 0.01 T) did not show strong decrease of the signal around 3 K, which is typical for the presence of even very small admixture of tin in the samples (superconductivity critical temperature for metallic tin is 3.7 K) [11].

Two ways of solvothermal synthesis of Sn_4P_3 were reported by the group of *Qian* [8]. In their first work [8a], the reaction between tin chloride $SnCl_2 \cdot 2H_2O$, potassium borohydride KBH_4, and yellow phosphorus P_4 was performed in absolute ethanol. The nonhomogeneous distribution of the nanoparticles of Sn_4P_3 was observed, which makes careful analysis of the XRD data difficult. However, the X-ray photoelectron spectroscopy study showed that the Sn:P ratio in the synthesized sample was 4.32:3, which is close to the stoichiometric ratio. The disadvantage of this synthesis is the use of highly air and water sensitive materials: yellow phosphorus spontaneously burns in air, while KBH_4 decomposes under the contact with water. The authors [8a] stated that the interaction of other different precursors, including the reaction between yellow phosphorus and metallic tin, did not lead to the formation of tin phosphides. As it shown in this work, the reaction of metallic tin with the less active modification of phosphorus, red phosphorus, in other solvent than ethanol, namely, ethylenediamine, results in the formation of Sn_4P_3 in very high yields. In another report of the same group [8b] the nanorods of tin phosphide Sn_4P_3 were synthesized by the solvothermal reaction in ethylenediamine. In that case, the two-step synthesis was performed. At the first stage sodium phosphide Na_3P was made by the reaction of metallic sodium and yellow phosphorus; at the second stage the reaction between tin chloride $SnCl_2$ and sodium phosphide Na_3P was carried out resulting in the formation of nanorods of Sn_4P_3. The byproducts of the reaction, such as NaCl, unreacted sodium phosphide, or phosphorus, were removed by subsequent washing with benzene, ethanol, and water. It was assumed [8b] that ethylenediamine played an important role in the formation of the nanorods due to its N-chelation properties and also served as a template. The disadvantage of working with metallic sodium is clear. Moreover, no rod-like particles formation was obtained in our synthesis using ethylenediamine (Fig. 4A). In addition, it was shown [10] that an N-donor ligand is not necessary for the solvothermal synthesis of Cu_3P phosphide, as was suggested earlier by Qian et al. [12]. However, the understanding of the mechanism of tin phosphide formation during solvothermal synthesis is quite important, since it opens the ways to the synthesis of new metal phosphides or to varying the sample morphology, i.e. fabrication of the nanoparticles. In light of this, one very important question appears, why even in the syntheses with large excess of phosphorus always only one metal-rich phosphide is formed? Actually, three other tin phosphides are known, namely, SnP, Sn_3P_4, and SnP_3 [6,13], each containing more phosphorus than Sn_4P_3. Furthermore, the latter two phosphides are stable at ambient conditions [13]. The similar result was observed for the hydrothermal synthesis of copper phosphide Cu_3P [10], where even in the case of the 30 times excess of phosphorus only one copper-rich phosphide was obtained. Again, according to the Cu–P phase diagram, another phosphorus-rich compound CuP_2 is stable at ambient conditions [13].

The SEM revealed that tin particles, which are present as an admixture in the sample **TP-3** (Fig. 4A, inset), have exactly the same shape and size as the initial tin metal powder used for the syntheses (Fig. 4C). This indicates that tin does not dissolve in ethylenediamine under the solvothermal conditions. In order to shed some light on this problem, a synthesis at higher temperature (300 °C) and longer reaction time (85 h) was performed (sample **TP-10**). One can expect that the increase of the temperature and duration of the reaction should lead to the enhanced yield of the product. But this was proved not to be the case. The product of the **TP-10** synthesis is one big drop-like piece of the metallic tin on top of which the reaction took place. XRD confirms that the powder from the top of the metallic drop is a mixture of Sn_4P_3 and, seemingly, amorphous phase – which is probably red phosphorus. As tin was placed into a vessel as a powder, one can assume that the melting of tin occurs during the reaction (melting point 232 °C). This is direct evidence that metallic tin does not dissolve in the subcritical ethylenediamine ($T_c \sim 320\,^{\circ}C$). A significant decrease of the tin surface area leads to considerably lower reactivity of the metal. Apparently, the mechanism of the reaction is the following: red phosphorus dissolves solely in ethylenediamine and the solution reacts with metal (tin in our case). During the reaction the metal-rich phosphide forms and does not further react with phosphorus, presumably due to kinetic reasons.

4. Conclusions

A bulk, polycrystalline, phase pure tin phosphide Sn_4P_3 was prepared from the elements, metallic tin and red phosphorus, by a convenient solvothermal reaction in ethylenediamine. The reported synthesis is much simpler than the solvothermal ways described in the literature, since it does not require the operations with toxic/high-sensitive precursors. The investigation of the influence of the duration and temperature of the solvothermal synthesis as well as the starting components ratio on the phase composition of the product has resulted in the optimization of the synthetic conditions, leading to the high-yield synthesis. The analysis of the synthetic data has led to the assumption that the formation of Sn_4P_3 proceeds through the reaction of the metallic tin with the solution of phosphorus in subcritical ethylenediamine.

Acknowledgments

Yu.V. K. and S. R. thank the FY2005 JSPS Postdoctoral Fellowships for Foreign Researchers. A.V.S. acknowledges the support of the Russian Foundation for Basic Research.

Appendix A. Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jssc.2006.08.012.

References

[1] (a) V. Pralong, D.C.S. Souza, K.T. Leung, L.F. Nazar, Electrochem. Commun. 4 (2002) 516–520;
  (b) D.C.C. Silva, O. Crosnier, G. Ouvrar, J. Greedan, A. Safa-Sefat, L.F. Nazar, Electrochem. Solid-State Lett. 6 (2003) A162–A165;
  (c) K. Wang, J. Yang, J. Xie, B. Wang, Z. Wen, Electrochem. Commun. 5 (2003) 480–483;
  (d) M.P. Bichat, T. Politova, J.L. Pascal, F. Favier, L. Monconduit, J. Electrochem. Soc. 151 (2004) A2074–A2081;
  (e) F. Gillot, S. Boyanov, L. Dupont, M.-L. Doublet, M. Morcrette, L. Monconduit, J.-M. Tarascon, Chem. Mater. 17 (2005) 6327–6337;
  (f) M.-P. Bichat, J.-L. Pascal, F. Gillot, F. Favier, Chem. Mater. 17 (2005) 6761–6771;
  (g) Y.-U. Kim, C.K. Lee, H.-J. Sohn, T. Kanga, J. Electrochem. Soc. 151 (2004) A933–A937;
  (h) Y.-U. Kim, S.-I. Lee, C.K. Lee, H.-J. Sohn, J. Power Sources 141 (2005) 163–166;
  (i) W.C. Zhou, H.X. Yang, S.Y. Shao, X.P. Ai, Y.L. Cao, Electrochem. Commun. 8 (2006) 55–59.

[2] (a) P. Clark, W. Li, S.T. Oyama, J. Catal. 200 (2001) 140–147;
  (b) D.C. Phillips, S.J. Sawhill, R. Self, M.E. Bussell, J. Catal. 207 (2002) 266–273;
  (c) C. Stinner, Z. Tang, M. Haouas, Th. Weber, R. Prins, J. Catal. 208 (2002) 456–466;
  (d) S.T. Oyama, J. Catal. 216 (2003) 343–352;
  (e) V. Zuzaniuk, R. Prins, J. Catal. 219 (2003) 85–96;
  (f) P.A. Clark, S.T. Oyama, J. Catal. 218 (2003) 78–87;
  (g) M. Nagai, T. Fukiage, S. Kurata, Catal. Today 106 (2005) 201–205;
  (h) Y. Shu, Y.-K. Lee, S.T. Oyama, J. Catal. 236 (2005) 112–121;
  (i) S. Yang, R. Prins, Chem. Commun. (2005) 4178–4180;
  (j) Y. Shu, S.T. Oyama, Chem. Commun. (2005) 1143–1145;
  (k) R.L. Halm, K.M. Chadwick, B.R. Keyes, US Patent 4,946,980;
  (l) K.M. Chadwick, R.L. Halm, US Patent 4,985,580.

[3] H.-G. von Schnering, W. Hönle, Chem. Rev. 88 (1988) 243–273.

[4] W.E. Buhro, Polyhedron 13 (1994) 1131–1148.

[5] S.L. Brock, S.C. Perera, K.L. Stamm, Chem. Eur. J. 10 (2004) 3364–3371.

[6] (a) O. Olofsson, Acta Chem. Scand. 21 (1967) 1659–1660;
  (b) P. Eckerlin, W. Kischio, Z. Anorg. Allg. Chem. 363 (1968) 1–9;
  (c) L. Haggstrom, J. Gullman, T. Ericsson, R. Wappling, J. Solid State Chem. 13 (1975) 204–207;
  (d) Y.B. Kuz'ma, S.I. Chikhrii, V.N. Davydov, Inorg. Mater. 35 (1999) 10–11.

[7] R. Binions, C.S. Blackman, C.J. Carmalt, S.A. O'Neill, I.P. Parkin, K. Molloy, L. Apostilco, Polyhedron 21 (2002) 1943–1947.

[8] (a) H.L. Su, Y. Xie, B. Li, X.M. Liu, Y.T. Qian, J. Solid State Chem. 146 (1999) 110–113;
  (b) Y. Xie, H. Su, B. Li, Y. Qian, Mater. Res. Bull. 35 (2000) 675–680.

[9] (a) L.G. Akselrud, P.Y. Zavalij, Yu.N. Grin, V.K. Pecharsky, B. Baumgarthner, E. Wölfel, Mater. Sci. Forum 133–136 (1993) 335;
(b) V. Petricek, M. Dusek, L. Palatinus, Jana2000. The Crystallographic Computing System, Institute of Physics, Praha, Czech Republic, 2000.

[10] J.A. Aitken, V. Ganzha-Hazen, S.L. Brock, J. Solid State Chem. 178 (2005) 970–975.

[11] C. Buzea, K. Robbie, Supercond. Sci. Technol. 18 (2005) R1–R8.

[12] (a) Y. Xie, H.L. Su, X.F. Qian, X.M. Liu, Y.T. Qian, J. Solid State Chem. 149 (2000) 88–91;
(b) H.L. Su, Y. Xie, B. Li, X.M. Liu, Y.T. Qian, Solid State Ionics 122 (1999) 157–160.

[13] Th.B. Massalski (Ed. in Chief), H. Okamoto, P.R. Subramian, L. Kacprzak (Eds.), Binary Alloy Phase Diagrams, second ed., ASM International, 1996.