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Synthesis of Single-Phase Sn_3P_4 by an Isopiestic Method

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Zaikina et al.[1] reported recently on the crystal structure of Sn_3P_4 and described its thermoelectrical properties. Sn_3P_4 crystallizes in the trigonal space group $R\bar{3}m$. The crystal structure is characterized by Sn atoms arranged in layers parallel to (001) linked by P_2 dumbbells exhibiting an extensive disorder of their orientation. Several synthesis conditions were tried by Zaikina et al.[1] to prepare pure Sn_3P_4, i.e., they used different experimental conditions such as various annealing temperatures and durations, quenching or slow cooling, pressing of starting materials into pellets, use of tin(IV) iodide as transport agent, as well as lead chloride or lead as fluxes. However, in no instance were the authors able to prepare monophasic Sn_3P_4. Even with their best optimized conditions, they always ended up with Sn_4P_3 as impurity phase along with Sn_3P_4. As a consequence, the physical properties could not be studied on samples consisting of pure Sn_3P_4. Even the authors conceded a possible small influence of the admixture on the investigated physical properties, i.e., the defects caused by inclusions of different amounts of Sn_4P_3 besides grain boundaries might be responsible for the thermal behavior of Sn_3P_4.

The crystal structure itself was determined by single-crystal X-ray diffraction supported by ^{119}Sn Mössbauer spectroscopy and electron diffraction HREM images.[1] The cell metrics and intensity distribution obtained from a powder pattern (although not from a single-phase sample) are in accordance with the single-crystal structure investigations. The applied synthesis methods caused extensive twinning as shown by Zaikina et al.[1] based on HRTEM images.

The question of nonstoichiometry of Sn_3P_4 has not been fully clarified so far. Zaikina et al.[1] compared the lattice parameters of this compound, determined from phase mixtures with overall compositions on either side of the stoichiometric composition, and found only very small differences, but this cannot rule out a certain nonstoichiometry due to the small size of the phosphorus atoms and the highly defective phosphorus sublattice. Already in an earlier study Olofsson[2] was unable to determine the exact composition of Sn_3P_4, which he called $Sn_{0.7}P$. Nevertheless, the author claimed to have obtained a powder pattern for $Sn_{0.7}P$ from a two-phase mixture of (Sn_4P_3+$Sn_{0.7}P$), although the corresponding detailed report by Wadsten (ref 8 in the paper by Olofsson[2]) has apparently never been published.

The very reason for the failure to obtain single-phase Sn_3P_4 is clearly due to loss of phosphorus because of its high vapor pressure under the conditions employed. However, this can be avoided by performing the synthesis under an optimum phosphorus vapor pressure in a temperature gradient, i.e., optimum conditions to prepare pure Sn_3P_4 or any other binary metal phosphide can be provided by the so-called isopiestic method where the sample, kept at a given temperature, is equilibrated with phosphorus vapor of well-defined pressure arising from a reservoir which is heated at a certain temperature lower than that of the sample.

This isopiestic method is a technique employed in the authors' laboratory for more than 30 years mainly to obtain partial thermodynamic data of binary or ternary intermetallic systems. However, it is also a suitable technique to provide optimum conditions for the preparation of more or less pure single-phase reaction products, as demonstrated by Richter and co-workers[3,4] for $RuZn_3$ and Pt_5Zn_{21}, as examples. In the present study, the method is applied to the Sn−P system.

The basic principles of the isopiestic method have been described repeatedly.[5,6] A schematic diagram of the experimental setup used in the present investigation is shown in Figure 1. The setup is essentially made of quartz glass: it consists of an outer tube of 32 mm O.D. with one end closed and the other end with a ground joint that can be connected to a vacuum pump. A graphite crucible with 25 mm O.D. is placed at the bottom serving as a reservoir for phosphorus. On top of the reservoir, a quartz glass spacer of suitable height is placed. Approx. 150−200 mg of pure tin samples is filled into graphite crucibles which are in turn placed inside graphite crucible holders. These holders have provisions for easy insertion of a quartz glass thermocouple well. About 10−15 of the holders are

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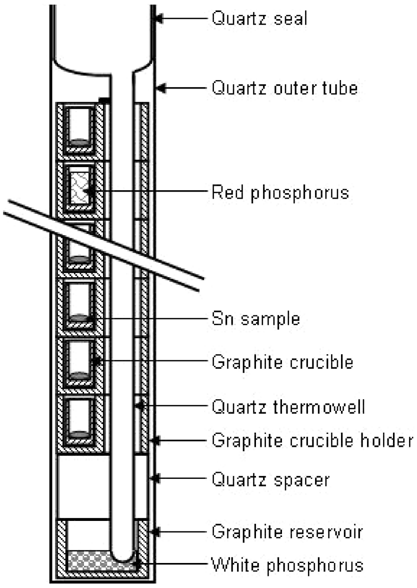

Figure 1. Schematics of isopiestic experimental setup.

stacked along the thermocouple well, with excess amount of red phosphorus placed in several of the holders at the top (which would recondense as white phosphorus in the reservoir during the experiment). The entire vessel is evacuated after repeated filling with Ar gas and sealed under a dynamic vacuum of less than 1×10^{-3} mbar. The isopiestic apparatus is then heated in a vertical two-zone furnace for a period of about 3 weeks. The temperatures of the samples (T_S) are measured by raising a Pt/Pt10% Rh thermocouple inside the thermocouple well. After equilibration, the isopiestic apparatus is quenched in water and cut open under Ar atmosphere in a glovebox. The individual samples (which have become Sn−P alloys during the equilibration) are weighed again and their compositions are derived from the mass difference which is attributed to the uptake of phosphorus. The samples are characterized by powder XRD on a Bruker D8 diffractometer in $\theta/2\theta$ geometry (reflection setting) equipped with a one-dimensional silicon strip detector using Cu Kα1 radiation (primary Ge-monochromator). The XRD patterns are analyzed and refined by means of the TOPAS 3 software (Bruker AXS, Germany) applying the fundamental parameter approach for peak profile modeling.

In all experiments, it is found that white phosphorus condenses in the reservoir at the lowest temperature (T_R). As the vapor pressure of white phosphorus is dominant over that of the red modification, the phosphorus vapor pressure in the apparatus is clearly defined by the temperature of the reservoir of white phosphorus. The results of two representative isopiestic runs, namely, one at low phosphorus pressure and another one at high phosphorus pressure, are given in Table 1; they are also shown in graphical form, superimposed on the phase diagram,[7] in Figure 2. It can be seen from Figure 2 that the compound Sn_3P_4 cannot be formed in pure form at the lower phosphorus pressure (41.5 mbar) in the temperature range employed. However, it can be formed at higher phosphorus pressures (280 mbar in this particular case) and is found to be stable in the temperature range of about 370−420 °C. A small nonstoichiometry of ~0.2 at % is observed in this temperature range. Above this temperature range, the compound looses phosphorus and transforms into Sn_4P_3 under the existing phosphorus vapor pressure.

Table 1. Results of Isopiestic Experiments; Standard State: P (white)

sample no.	P (at %)	T_S (°C)	phases
		Run 1[a]	
1	50.23	345	$Sn_4P_3 + Sn_3P_4$
2	43.49	364	Sn_4P_3
3	43.16	387	Sn_4P_3
4	43.23	414	Sn_4P_3
5	43.09	443	Sn_4P_3
6	42.93	473	Sn_4P_3
7	5.69	514	liquid
8	5.24	558	liquid
9	4.30	592	liquid
10	4.28	627	liquid
11	4.53	661	liquid
12	3.32	697	liquid
		Run 2[b]	
1	65.50	359	$Sn_3P_4 + SnP_3$
2	57.42	377	Sn_3P_4
3	57.33	393	Sn_3P_4
4	57.20	410	Sn_3P_4
5	43.00	429	Sn_4P_3
6	43.12	451	Sn_4P_3
7	43.19	474	Sn_4P_3
8	38.55	503	liquid + Sn_4P_3
9	6.64	528	liquid
10	5.00	554	liquid
11	6.43	583	liquid
12	5.87	622	liquid
13	4.52	651	liquid

[a] T_R = 153 °C, P_{total} = 41.5 mbar; 24 days. [b] T_R = 218 °C, P_{total} = 280 mbar; 26 days.

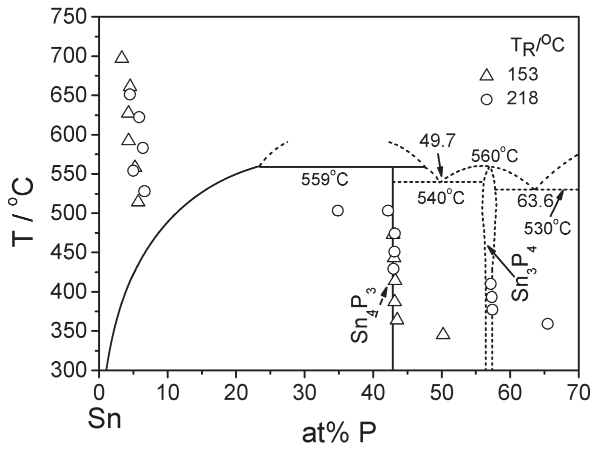

Figure 2. Sample composition vs sample temperature for two isopiestic experiments with reservoir temperatures T_R = 153 °C (Δ) and T_R = 218 °C (○) corresponding to phosphorus pressures of 41.5 and 280 mbar, respectively.

The XRD pattern of the obtained Sn_3P_4 and the structural parameters of the Rietveld refinement are given in Figure 3 and Table 2, respectively. The atomic

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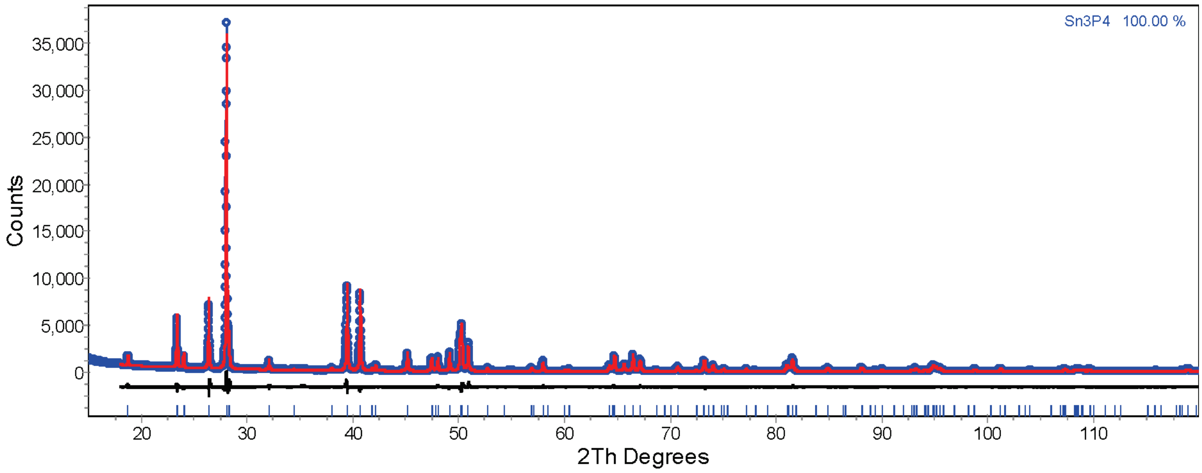

Figure 3. Experimental XRD pattern of Sn_3P_4 (blue circles) in comparison to the refined powder pattern (red line). The difference curve is shown as a black line. The blue ticks along the x-axis are the calculated Bragg positions.

Table 2. Results of Rietveld Refinement for Sn_3P_4 (Sample 4, Run 2)

R_p/R_{wp}	7.2/9.54
background	Chebychev, third order
specimen displacement (mm)	−0.0207(5)
structure type	Sn_3P_4
space group/Z	$R\,3\overline{m}/3$ {Sn_3P_4}
fraction (%)	100
a (Å)	4.4311(1)
c (Å)	28.3927(3)
cell volume (Å^3)	482.81(1)
crystallite size (Lorentzian, nm)	401(14)
strain L	0.1508(24)
2θ range (deg)	18−120
preferred orientation	none

site	multiplicity and Wyckoff letter	x	y	z	occupancy	B(iso) (Å^2)
Sn1	3*a*	0	0	0	1	1.54(2)
Sn2	6*c*	0	0	0.79443(3)	1	1.54(2)
P1	6*c*	0	0	0.4293(4)	0.266(6)	1.16(10)
P2	6*c*	0	0	0.3563(4)	0.261(5)	1.16(10)
P3	18*h*	0.206(1)	$-x$	0.0767(3)	0.267(4)	1.16(10)
P4	18*h*	0.135(1)	$-x$	0.3869(3)	0.251(4)	1.16(10)

coordinates of our refinement are in excellent agreement with the structural model given by Zaikina et al.,[1] and the pattern was found to be pure Sn_3P_4 without any detectable traces of Sn_4P_3 or SnP_3. The site occupation factors of the P atoms are slightly enlarged resulting formally in the composition $Sn_3P_{4.16}$. Because of too short interatomic P−P distances, it has to be considered as an artifact of the refinement. Detailed phase equilibria and a thermochemical analysis of the Sn−P system are beyond the scope of the present communication and will be reported elsewhere.

In summary, the isopiestic technique can be employed to provide optimum conditions for the formation of a binary or ternary target compound in which one of the components is volatile. After establishing the optimum condition, the method could even be employed for bulk synthesis or commercial production of metal phosphides, which are considered potential candidates in semiconducting electronics, in catalysis, as anode materials, etc.[8]

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