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SnP

The Synthesis, Structure, and Superconducting Properties of New High-Pressure Forms of Tin Phosphide

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Reactions of Sn and P in a tetrahedral anvil press at conditions ranging from 15 to 65 kbars and 600 to 1300° gave intimate mixtures of two new forms of SnP: a tetragonal form having cell dimensions $a = 3.831 \pm 0.001$ Å and $c = 5.963 \pm 0.001$ Å and a cubic rock salt type having $a = 5.5359 \pm 0.0001$ Å at 25°. The crystal structure of the tetragonal phase was refined from powder diffraction intensity data and shown to be similar to that of high-pressure GeP and GeAs. The tetragonal form transformed slowly and irreversibly to the cubic form when heated at ambient pressure between 100 and 200°. Meissner-effect measurements showed the tetragonal form to be normal to 1.25°K and the cubic form to be superconducting between 2.8 and 4.0°K.

Introduction

In the Sn–P system, only the compounds SnP[1] and Sn_4P_3[2] are known. Both have hexagonal crystal structures. Osugi, *et al.*,[3] reported the formation of sphalerite-type SnP at 1600–1800° and 40–50 kbars. The powder pattern,[4] however, was the same as that reported herein for NaCl-type SnP.

Experimental Section

All reactions were run in a tetrahedral anvil press of National Bureau of Standards design[5] using a cylindrical boron nitride crucible approximately 0.6 cm long and 0.125 cm^3 in volume, surrounded by a graphite-sleeve resistance heater inserted in a pyrophyllite tetrahedron. The temperature was measured using a Pt–Rh thermocouple uncorrected for pressure effects and placed at the center of the surface of the cylinder. The temperature at the ends is approximately 30% lower. The operating procedure has been explained elsewhere.[6]

High-purity Sn filings were obtained from a metal rod and passed through a magnet to remove impurity from the file. These were mixed with powdered P and pelleted. Several reactions were run at various conditions. In general, the reactants were cold pressured, then brought to temperature, held for 1 or 2 hr, cooled for about 2 hr, and quenched to room temperature in less than 1 min while pressure was maintained.

All products were characterized by Debye–Scherrer X-ray powder diffraction at 25°. Films were read on a David Mann film reader, Model No. 1222. Unit cell dimensions were refined by a least-squares method with the Nelson–Riley function as one parameter.

Electrical resistivities were measured by a four-probe technique described previously.[7] Superconducting transition temperatures were measured by observing the Meissner effect at temperatures above 1.25°K.

Results

Filings of Sn were mixed with powdered P in the Sn:P atomic ratio of 1:(0.9–1.1) and treated at the conditions of 800° and 65 kbars, holding 1 hr, cooling 3 hr to 500°, and quenching. Reactions were also run at 1200° and 65 kbars and at 900° and 15 kbars. The products of all reactions showed similar Debye–Scherrer patterns. Two phases were present, a major tetragonal phase and a minor cubic phase. The Debye–Scherrer pattern of the major phase (Table I) was indexed on the basis of a tetragonal cell: $a = 3.831 \pm 0.001$ Å, $c = 5.963 \pm 0.001$ Å. The weaker lines were indexed on the basis of a cubic cell: $a = 5.5359 \pm 0.0001$ Å. The reflections of the cubic cell were analogous to those of SnAs[8] but shifted to indicate a smaller cell.

The mixture of tetragonal and cubic phases, when heated in air at ambient pressure, transformed slowly and irreversibly to the cubic phase between 100 and 200°. A broad, shallow endotherm was seen in the dta of several samples. On a few samples the transition could not be seen in the dta.

Resistivity measurements on a polycrystalline piece of SnP which was composed predominantly of the tetragonal form showed metallic behavior: $\rho_{25°C} = 2 \times 10^{-5}$ ohm cm, $\rho_{4.2°K} = 3 \times 10^{-6}$ ohm cm. Meissner effect was measured on both the tetragonal and cubic forms. The tetragonal form did not show a superconducting transition to 1.25°K; the cubic form showed a superconducting transition temperature between 2.8 and 4.8°K.

Experiments under similar conditions but starting with an Sn:P ratio of 1:2 generally yielded the same mixture of tetragonal and cubic SnP and black P.

Crystal Structure Analysis

The crystal structure of the tetragonal phase was refined from powder intensity data. The structure is similar to that of high-pressure GeP and GeAs.[9] Intensity data were gathered from a diffractometer tracing by obtaining relative weights of the peaks. A Norelco diffractometer using Cu Kα radiation and a LiF bent crystal monochromator was used. A scanning rate of 0.25°/min was used with the chart scaled to 1 in./deg. A smooth background curve was drawn and the peaks were traced onto Cronaflex drafting film.

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