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A Method for Growing Single Crystals of Metallic Indium Antimonide under Pressure

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A method is described for growing single crystals of the metallic β-tin phase of InSb. These crystals were grown from the melt at a pressure of 26 Kbars and recovered, in their metastable state, at liquid-nitrogen temperature. They were cylindrical in shape with lengths ranging from 6–20 mm and diameters ranging from 3–6 mm.

The phase diagram of InSb has been studied by Jayaraman *et al.*[1,2] and Hanneman *et al.*[3] who showed that the transition to metallic InSb occurs near 23 Kbars at room temperature and that the transition pressure depends only slightly on temperature. This solid–solid transition has a large change in volume associated with it ($\approx$20%). Jayarman found that the transition was very sluggish at room temperature but became much sharper at higher temperatures. Jamieson[4] subsequently showed that the crystal structure of this phase was very close to, if not identical with, that of white tin. More recently, several people[5–7] have found that the phase of InSb stable at pressures above 30 Kbars has an orthorhombic, rather than β-tin structure.

Darnell and Libby[8,9] have developed a technique for removing InSb, in its metallic β-tin phase, from the high-pressure chamber. This was done by heating and compressing the material well into the region of the P–T diagram where the metallic β-tin phase is thermodynamically stable. The material was then cooled, while under pressure, to liquid-nitrogen temperatures, at which point the pressure was reduced to one atmoshpere and the sample removed. The material so obtained has been identified as having the β-tin structure with lattice parameters essentially identical to those of β-tin.

We will describe in this paper a method for growing single crystals of the metallic β-tin phase of InSb under pressure and recovering them at one atmosphere. The crystals so obtained were cylindrical in shape with lengths ranging from 6–20 mm and diameters ranging from 3–6 mm.

The press used in this work was of the piston-cylinder hydraulic-ram type very similar to the one described by Kennedy and La Mori.[10] A schematic diagram of the pressure chamber with the pressure cell in position is shown in Fig. 1. An aluminum trough was pressed around the outside of the retaining rings and was filled with liquid nitrogen when it was desired to cool the sample.

Figure 2 shows the details about the pressure cell. This figure is self-explanatory with regard to the materials used and their dimensions. The starting material was semiconducting grade n-type polycrystalline indium antimonide obtained from Cominco Products, Inc.

The sample was first molded into a cylindrical shape with one of its ends tapered to a point. The mold material was a high-purity, fine-grained graphite obtained from Poco, Inc. The molding process was done under vacuum using a vertical tube furnace. The sample and mold were then fitted into an insulating cylinder made of talc which in turn was fitted into a cylindrical

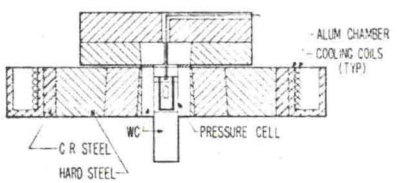

FIG. 1. Press chamber with cell in place.

graphite tube furnace with a tapered wall thickness. This assembly was adjusted so that the pointed end of the sample was near the thick end of the furnace. The furnace was then surrounded with a talc sheath. These components together with a stainless steel cap and pyrophyllite pressure seal constitute the pressure cell assembly. A $\frac{1}{16}$ in. diameter hole was drilled through the steel cap and into the talc so that a chromel–alumel thermocouple, encased in a 2-holed mullite tube, could be placed about 2 mm above the pointed end of the sample. A 5 kVA transformer controlled by a motor-driven powerstat in the primary circuit supplied power to the resistance furnace.

This pressure cell differs from the normally used cell in having a furnace with a tapered rather than uniform wall thickness. The furnace was tapered so as to provide a temperature gradient along its length; the thicker end being at a lower temperature. The sample, upon being cooled from the liquid phase, solidifies first at its pointed

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[10] G. C. Kennedy and P. N. LaMori, *Progress in Very High Pressure*, F. P. Bundy, W. R. Hibbard, Jr., and H. M. Strong, Eds. (John Wiley & Sons, Inc., New York, 1961).

end which acts as the nucleation center for the crystal growth process. The solid–liquid phase boundary thereafter travels down the length of the sample. This is essentially the Bridgman method of growing single crystals. The rate of growth is controlled by the motor driven powerstat. The temperature gradient was determined by making several dummy runs with thermocouples, sealed in boron-nitride tubes, placed at various positions along the length of the sample. The gradient was found to be fairly linear between 7 and 20 mm from the thick end of the furnace. It ranged from 20°–30°C/cm for furnace temperatures between 300° and 400°C.

Before inserting the cell into the pressure vessel, the vessel was lubricated with dry molybdenum disulfide power and the cell wrapped in a 0.002 in. layer of lead foil to decrease friction between the cell and vessel walls.

The sample was first pressurized to 25 Kbars for about 12 h. It was then heated until the thermocouple, which was at the cooler end of the furnace, read 400°C. The sample was kept at this temperature for one hour in order to make certain that it was entirely in the liquid phase. The pressure was then set at 26 Kbars. The starting pressure was very important since starting with too high a pressure would cause the sample, upon cooling, to enter a region where both the orthorhombic and β-tin phases are in equilibrium. The resulting sample would then be composed of a mixture of the two phases. On the other hand, if the starting pressure was too low, the sample would revert back to the zinc-blend phase upon cooling. This would occur because there is a pressure drop of 2–3 Kbars due to the thermal contraction of the oil and press materials. This could have been overcome by increasing the pressure while the crystal was being cooled. However, it was feared that this would further strain the crystal. The press controls were never touched once the crystal growth process was started. The crystal was grown by using the motor driven powerstat to slowly reduce the power being supplied to the furnace. The most successful growth rate was estimated to be about 5 cm/h.

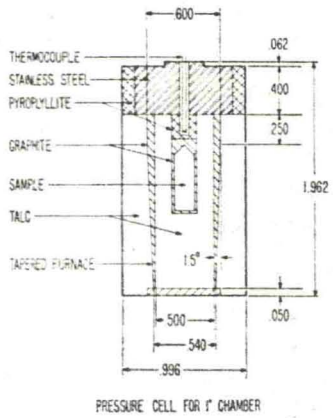

FIG. 2. Pressure cell for 1 in. chamber.

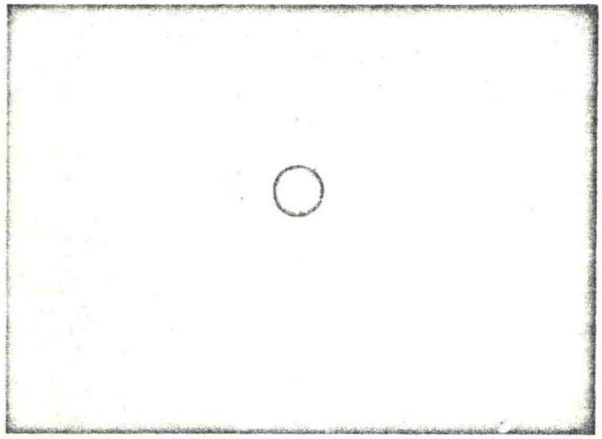

FIG. 3. Laue photo of InSb single crystal.

Once the crystal was grown, the temperature was further reduced to about 150°C at which point the driving motor was turned off and the crystal allowed to anneal at this temperature for two–three days. The temperature was then reduced to room temperature and liquid nitrogen introduced into the aluminum trough surrounding the pressure chamber. The crystal could only be cooled to about −125°C due to the large thermal path that the steel backup plates provided. The pressure was then reduced to one atmosphere over a period of four or five hours. The crystal was then removed from the press and stored in liquid nitrogen.

X-ray studies were made of these crystals using a Polaroid Laue camera with a Picker x-ray diffraction unit. Since the crystals could not be etched, the x-ray photos were not of the highest quality. However, it was easy to identify the major symmetry axes and confirm that the crystal had the β-tin structure. A typical x-ray Laue pattern is shown in Fig. 3. In order to verify that the crystals were indeed single, x-ray Laue shots were taken at 2 mm intervals as the crystal was translated horizontally from one end to the other without changing its orintation. The resulting Laue patterns were identical in every respect. Thus, it was concluded that the samples were indeed single crystals.