

THE PREPARATION AND CHARACTERIZATION OF CRYSTALS OF
THE SUPERCONDUCTING POLYMER, $(\text{SN})_x$

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ABSTRACT

A technique is described for growing $(\text{SN})_x$ crystals which have superior electrical properties to those reported previously. The room temperature electrical conductivity has increased, so has the ratio of the room temperature and 4°K resistivities. There is no conductivity maximum in the region 20-30°K and the superconducting transition temperature is higher.

Introduction

Polysulfur nitride or polythiazyl $(\text{SN})_x$ has been known since 1910 when Burt (1) prepared it in the form of films and crystals. However, it was only recently that its structure was determined (2,3) and the physics of this polymer began to be investigated. A variety of recent experiments (4-8) have indicated that $(\text{SN})_x$ is an anisotropic metal. In addition it has been shown to be a superconductor with a transition temperature near 0.3°K (8). In all this published work the role of the crystal perfection and chemical purity has been questioned. Here we report the preparation and characterization of $(\text{SN})_x$ crystals which have significantly better electrical properties than those reported earlier. This suggests that the crystal quality has been substantially improved by our preparative techniques.

Preparation

Current techniques for the preparation of $(\text{SN})_x$ usually involve the solid state polymerization of S_2N_2 which is obtained by the thermal splitting of N_4S_4 . This latter reaction has been studied by various authors (9,10). We prepared N_4S_4 by the method described in the literature (11) and carefully purified it by recrystallization from benzene followed by vacuum (10^{-5} torr) fractional sublimation. The resulting N_4S_4 had a melting point of 189°C which is some 10° higher than the normally quoted melting point and reflects the high degree of purity (1,11). Chemical analysis gave S, 70.15%; N, 29.86% (calculated, S, 69.59%; N, 30.41%). X-ray studies showed it to be single phase with excellent agreement between the calculated and experimental powder diffraction patterns. This purified material was stored in vacuum prior to

being used to prepare S_2N_2 . The N_4S_4 was heated to $\sim 80^\circ C$ and the vapor passed over silver wire heated to $\sim 325^\circ C$ using the apparatus shown in Fig. 1. Prior to heating the N_4S_4 the vacuum was 10^{-5} torr, however, during the initial stages of the reaction nitrogen is produced and the pressure rises. The remaining condensible products of the thermal splitting of N_4S_4 are

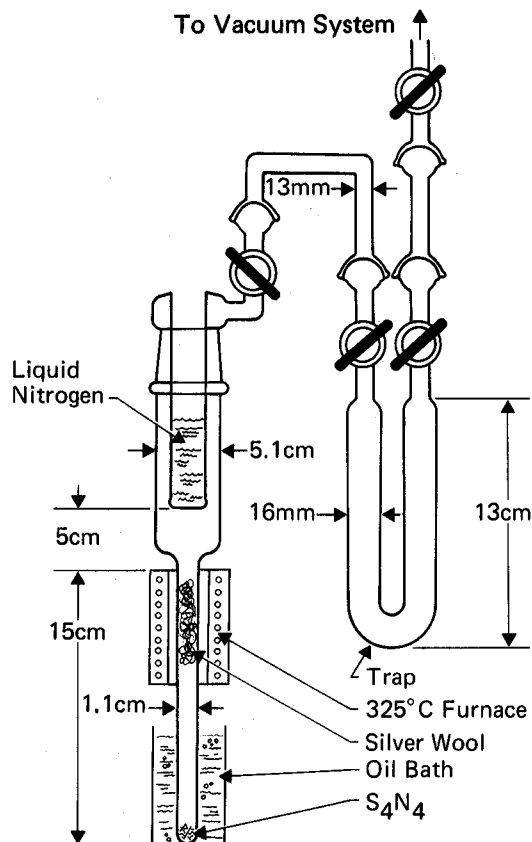


FIG. 1
Apparatus for Preparation of
(SN)_x Crystals

trapped out on the liquid nitrogen cooled cold finger together with some N_4S_4 which either did not react or re-formed from S_2N_2 in the vapor phase. After all the N_4S_4 had evaporated both sources of heat were removed and the cold finger was allowed to slowly warm up to room temperature and the most volatile product N_2S_2 was pumped into the liquid nitrogen cooled U-tube. The evacuated U-tube was then isolated from the vacuum system and the liquid nitrogen was replaced by ice. This ice bath was maintained for a period of approximately five days. During this time the resulting S_2N_2 crystals slowly polymerized to give $(SN)_x$ crystals in the form of needles 5-10mm long and 0.5mm wide and also as more equidimensional crystals. The crystals were shaped like distorted hexagons about the b or needle axis. This habit is determined by the principal cleavage planes observed by Boudeulle (2). Many of the crystals also had well shaped faces at angles to the needle axis. Before removing the crystals; the U-tube was pumped on continuously for a period of 24 hours at a vacuum of 10^{-5} torr, in order to remove any unpolymerized S_2N_2 .

Characterization

General

Chemical analysis of these brass-colored $(SN)_x$ crystals gave S, 69.62%;

N, 30.63% (calculated S, 69.59%; N, 30.41%). The material gave no ESR signal at 4°K or 300°K which suggests that there are only a small number of chain ends, i.e., the chains are long. X-ray measurements on compressed samples gave a combination of sharp and broad peaks expected for a fibrous material. There were no indications of second phases. Differential thermal analysis in a helium atmosphere showed no phase changes between liquid nitrogen temperature and 200°C. At $\sim 233^\circ\text{C}$ an endothermic peak is observed which is associated with complete vaporization of the $(\text{SN})_x$. Thermogravimetric analysis showed that vaporization began around 125°C. In air this process became strongly exothermic. This result is consistent with the observation that on vigorous grinding or on compressing in air $(\text{SN})_x$ frequently exploded. We believe this is an intrinsic property of the $(\text{SN})_x$ and that it is not due to the presence of S_2N_2 .

Mass spectroscopic data obtained using a beam energy of 70 K eV and a sample temperature of 150°C showed that the principal species obtained on vaporizing $(\text{SN})_x$ were N_2 , S, SN and S_2N_2 . No species corresponding to large polymeric chains were obtained; the largest mass species observed was S_4N_4 .

Scanning Electron Microscopy

The scanning electron microscope pictures in Fig. 2 clearly show these crystals to be bundles of fibres running parallel to the chain direction (b-axis). This twinned crystal was chosen despite its imperfect nature because it clearly illustrates the general nature of these $(\text{SN})_x$ crystals. Fig. 2a shows the twin itself and Fig. 2b shows the fibres running parallel to the b-axis of each crystal and meeting at the line of intersection between the two crystals. The ends of the fibres which terminate on the faces

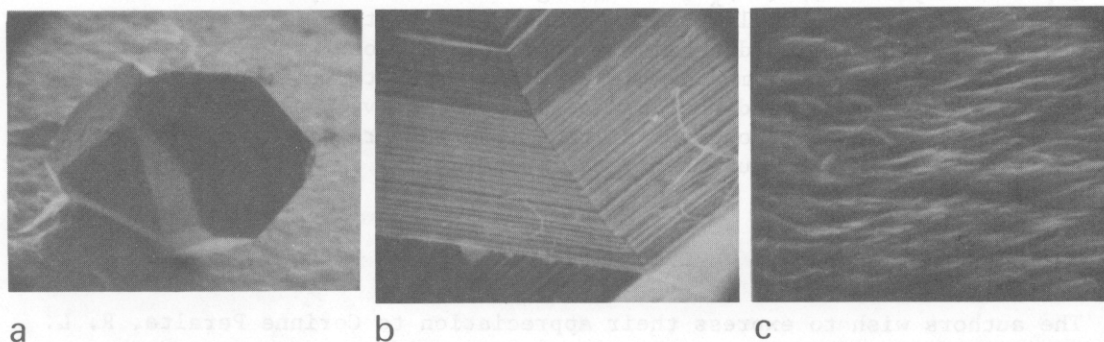


FIG. 2

- (a) Twinned crystal of $(\text{SN})_x$ magnified 20 times.
- (b) Fibres parallel to b axis of each crystal magnified 250 times.
- (c) Fibres terminating on faces at angles to b axis magnified 2,400 times.

at angles to the b axis are shown in Fig. 2c. From these and other pictures it is estimated that the individual fibres are less than 2000Å in diameter. In contrast to this crystal, others have optically smooth surfaces and these crystals have been suitable for specular reflectance studies (12). Nevertheless under high magnification their fibrous nature is revealed.

Electrical Properties

The most direct evidence that $(\text{SN})_x$ crystals grown by our techniques are significantly better than reported in previous work comes from their electrical properties. We find that the d.c. conductivity along the fibre axis of an average crystal increased from $\sim 600 \Omega^{-1}\text{cm}^{-1}$ to $2000 \Omega^{-1}\text{cm}^{-1}$. More significantly we find that the ratio of the resistivity at room temperature to that at 4°K is consistently greater than 100 and the resistivity minimum previously found (4,7) between 20 and 30°K is absent. The largest resistivity ratio previously reported (7) was 25 and the average was ~ 10 . These results clearly suggest either that our new crystals have fewer impurities or that the average polymer chain length has increased. We favor the latter interpretation. Though SEM studies show our crystals are still fibrous we do believe that their degree of perfection is considerably improved by this technique. In addition to the change in the normal state electrical conductivity we find that the superconducting transition temperature is also sensitive to the crystal quality. These improved crystals have a superconducting transition temperature of 0.33°K compared to 0.26°K for the previous crystals. The width of the superconducting transition has decreased from 0.08°K to 0.06°K . As was the case for most of our previous crystals there is no measurable residual resistance in the superconducting state. These results suggest that the transition temperature would be even higher if crystals with longer, more defect free chains could be prepared. It is well known that the transition temperature can be depressed by disorder as in the Al_5 compounds (13) or by a defect induced reduction of an energy gap anisotropy (14).

Summary

Improved crystals of $(\text{SN})_x$ have been grown. These crystals are still fibrous, however, electrical measurements suggest that the purity or degree of perfection along the needle axis is superior to those grown by other techniques. This is confirmed by higher room temperature conductivity, larger resistivity ratio and the absence of a resistivity minimum in the region 20 - 30°K . The superconducting transition temperature is also shown to be sensitive to the technique of crystal preparation.

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