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790

TITLE Acceptor Dopants for Lead Telluride

PROGRAM
SNAP 10A

SUBACCOUNT TITLE
TE Materials Development

STATEMENT OF PROBLEM The P-type PbTe used in SNAP 10A exhibits properties inferior to those of N-type material. The most probable causes of the inferior properties are: (1) the chemical character of the dopant used (sodium) and, (2) the associated non-stoichiometry.

ABSTRACT

Alternative P-type dopants were studied, namely, thallium, phosphorus, and arsenic. Ingots were grown from a melt containing one atom percent dopant and their electrical properties evaluated. Also, sintered pellets of PbTe were doped by exposure at high temperature to gaseous dopants. In most cases, the doping concentrations obtained were insufficient for SNAP 10A requirements. In one instance, however, namely arsenic doping of tellurium-rich PbTe, the desired heavy doping was obtained. These preliminary studies suggest that dopants other than sodium might be suitable for SNAP 10A requirements.

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Introduction

Doping of PbS type semiconductors has been studied extensively over the past ten years. Of these compounds, the most studied is PbS itself. A lengthy account of this work has been given by Bloem,[1] and shorter descriptions by Thomas[2] and Hutson.[2] The picture that results from these investigations differs significantly from the well-known picture of the elementary semiconductors, Ge and Si, where the doping usually depends only on the chemical impurities present. By contrast, the doping of PbS depends strongly upon both (1) the chemical impurities present and (2) the stoichiometry of the compound. The two doping effects have been compared quantitatively in PbS by measurements of the relevant chemical constants for each doping effect.[1,2]

In the case of PbTe, doping behavior is not understood so quantitatively, but does appear to be similar to the PbS case. Kovalchik and Maslakovets[3] have reported the effect of several chemical impurities for various deviations from stoichiometry in PbTe. The most extensive accounts appears in the Fritts patents[4] which cover many chemical impurities for the stoichiometric and Pb-rich cases. The Fritts patents indicate, for the case of stoichiometry, that the strongest P-type doping is obtained with sodium. Furthermore, as reported in these patents, only sodium and similar alkali elements are likely to afford the heavy doping required in the SNAP 10A application. Nevertheless, the possibility remains that under tellurium-rich conditions, other dopants may provide sufficiently heavy P-doping. The present investigation was undertaken to explore this possibility.

Several experiments were started in this work, though none had yet obtained anything like complete answers, the time the project was cancelled. The present report may serve as a useful record should the question of P-doping of PbTe be raised again.

Preliminary Experiments with Sintered Pellets

A preliminary test of the possibility of obtaining heavy doping with these elements was made with sintered pellets from SNAP. The pellets were N-type, doped with PbI, and of unknown stoichiometry.

The doping procedure went like this: A pellet was cleaned and loaded into a quartz capsule with a quantity of dopant calculated to give an initial vapor pressure of one atmosphere at 800°C. The capsule was sealed off under a vacuum of about one micron and then heated at 800°C for a specified time. After the 800°C treatment, the capsule was partially removed from the furnace and a wet cloth applied to the exposed end of the capsule to condense vapors onto the quartz. In this way the pellet was kept free of condensate. After about one minute of this "cold finger" treatment, the capsule was quenched in water.

When phosphorus was used as dopant in a 100-hour run, the pellet remained N-type. However, with arsenic as dopant, the entire pellet converted to P-type.*

Thus arsenic appeared the more promising of these two acceptor dopants and hence was studied the more intensively.

Preparation of Doped Ingots by the Bridgeman Method

Considerably more information on doping effects can be obtained from materials prepared by zone melting techniques. The Bridgeman technique used here, for example, enables one to study a range of doping conditions with each ingot grown. Thus in an exploratory investigation like the present one, various compositions can be scanned rather rapidly for the parameters of interest. The compositions involved in the present case are illustrated schematically in Fig. 1.

Recipes for the Bridgeman growth of PbTe have been given by Brady.[5] The present procedure followed Brady[5] in most respects. We used quartz capsules of about 1/2" I.D. and 6" length. The capsules were baked in hydrogen at $\sim$1000°C for $\sim$30 minutes, and the inside bottom half of the capsule was coated with pyrolyte graphite formed by decomposing acetone vapor at $\sim$1000°C.

The chemicals used were the highest purity available from ASARCO (American Smelting and Refining Co.), reportedly $\sim$ 99.999% pure, with the

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*Indeed resistivity measurements with an improvised 4 point probe indicated all portions of the converted pellet to have a resistivity $\rho \sim 10^{-2}\ \Omega$ cm. Thus concentration gradients in the arsenic appear to decay in a 100 hour run. If the decay occurred solely by solid state diffusion, the diffusivity of the arsenic would be about 10^{-6} cm^2/sec, which seems unreasonably large. Thus, probably the porosity of the sintered pellet assists the arsenic transport.
On the other hand, a pellet exposed to arsenic vapor as above, but only for one hour, converted to a depth of only about one millimeter. The apparent diffusivity for this process is again about 10^{-6} cm^2/sec.

exception of phosphorus. The phosphorus used was kindly supplied by F. Pizzarello of Hughes Aircraft Company and had been doubly distilled from high purity phosphorus of the American Agricultural Co.

Weighed amounts of the appropriate chemicals were loaded into the quartz capsule, which was sealed off at ~1μ pressure. The capsule was then suspended vertically in a tube furnace at ~950°C and left overnight to insure mixing. The capsule was then lowered out of the furnace at ~0.4"/hr. The ingots were ~2" long in every case.

Evaluation of the Doped Ingots

The Bridgeman-grown ingots just described were evaluated principally by means of resistivity measurements. In one instance (the thallium-doped ingot) Seebeck coefficients were also measured and found to be consistent with the measured resistivity. Some observations of crystal quality were also made and will be described briefly.

The first ingot grown was thallium-doped under stoichiometric conditions. The ingot was cut into four slugs of equal length, and measurements of resistance and Seebeck coefficient were made by J. Morris with the results tabulated below:

Slug	Resistance ("cap to cap") μ-Ω	Calculated Resistivity Ω cm	α μv/°C
Nose	(Cleaved during handling)		204
2nd	2470	0.0021	180
3rd	4020	0.0033	171
Tail	3460	0.0029	152

This ingot was entirely P-type, and exhibited small variation in properties along its length.* The lowest resistivity observed, namely 0.002 Ω cm, is approximately the minimum resistivity value reported by Fritts[4] for Te-doped PbTe.

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*A more detailed study of subsequent ingots brings out appreciable lengthwise variations in properties. Figs. 1, 2, and 3.

A phosphorus-doped ingot was also grown under stoichiometric conditions. This ingot was entirely P-type. Thus phosphorus, which was not included in earlier doping studies, is evidently a P-type dopant. It is not as effective as thallium, however, as the lowest resistivity obtained with phosphorus was 0.003 cm. (This and subsequent resistivity measurements were made with a "Theco" four point probe, which our laboratory had just received.)

Next an arsenic-doped ingot was grown, again under stoichiometric conditions. In this case, the nose of the ingot was high resistivity N-type. Thus in terms of Fig. 1, the first solid material to freeze must have been fairly far to the left (or Pb-rich) side of the solidus field. The resistivities measured along the length of this ingot are shown in Fig. 2. The lowest resistivity obtained was 0.002 cm, which agrees with Fritts[4].

A second arsenic-doped ingot was grown, using this time a lead-rich melt. The melt composition was 49.5% Pb, 49.5% Te, and 1% As. The resulting ingot was entirely N-types. This is a case where stoichiometry "overrules" the dopant.

Lastly an arsenic-doped ingot was grown from a tellurium-rich melt. The melt composition was 49.35 % Pb, 49.65% Te, and 1% As. The resulting ingot was entirely P-type and exhibited the lowest resistivity in this investigation, namely 0.0008 cm. The resistivity profile for this ingot is shown in Fig. 3.

A brittle region was present about halfway along this ingot. The same was true of the stoichiometric, arsenic-doped ingot. These brittle regions could have occurred from any of a number of causes, under the crude experimental conditions employed here.

Although many parameters were uncontrolled during crystal growth (e.g. the rate of cooling of the solidified material), nevertheless ingots of fair quality were obtained. The nose slug of the thallium-doped ingot, which had cleaved, was used for an X-ray study of crystal orientation by K. T. Miller and P. Romo. Laue reflections were observed from several locations on the "cleaved" surface and indicated that the ingot was composed of crystallites of approximately the same orientation, i.e. all lined up within about 2°.

Discussion and Conclusions

The original object of this investigation was to characterize chemical equilibria for several acceptor dopants in PbTe. For example, we wanted to relate the concentration of off-stoichiometry defects to the solubilities of the acceptors. However, such studies are lengthy and only the preliminary survey portion of the work was completed in the time the project existed.

The survey work included several acceptor elements under stoichiometric conditions in addition, one acceptor was studied under off-stoichiometric conditions. Thus some idea of the relative importance of stoichiometry and chemical identity of dopant was obtained. It would appear that stoichiometry is no less important than the proper choice of dopant.

In terms of the specific problem stated at the beginning of this TDR then, it would appear that heavily P-type PbTe must be tellurium-rich, whatever the particular dopant used. Thus even though one were to substitute arsenic for sodium in the P-type pellets used in SNAP 10A, this material would still have to be tellurium-rich. Only this qualitative statement can be made here; we do not have enough data to judge quantitatively how tellurium-rich the material need be.

The present survey work was also quite limited. Other work[6] has shown how heat treatment can drastically affect the attainment of equilibrium in undoped PbTe. Very likely these heat treatment effects are also important in the doped material, but we did not check this point.

The principal point that was tested in this survey was the possibility of heavy doping with dopants other than the alkali metals. It was shown that at least one acceptor dopant, namely arsenic, can afford the same heavy doping the sodium dopant presently used.

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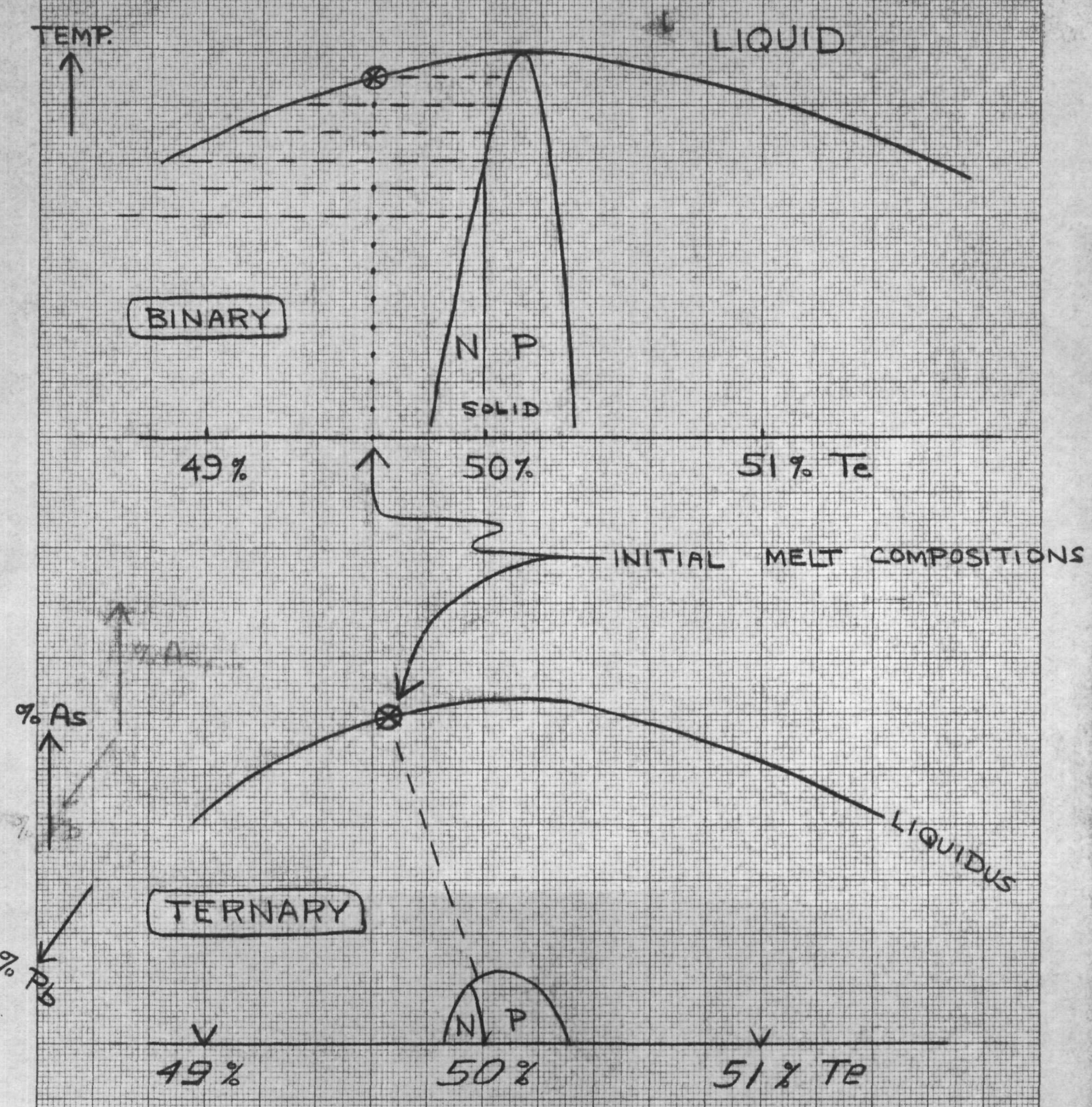

Figure 1. The Compositions Produced by Solidification from an Off-Stoichiometric Melt.

In the binary case a Pb-rich melt is shown; initially it yields P-type PbTe, and at lower temperatures produces N-type material. The ternary case is somewhat more complicated, but also can cause type changes during the course of solidification. (Tie lines are shown dashed.)

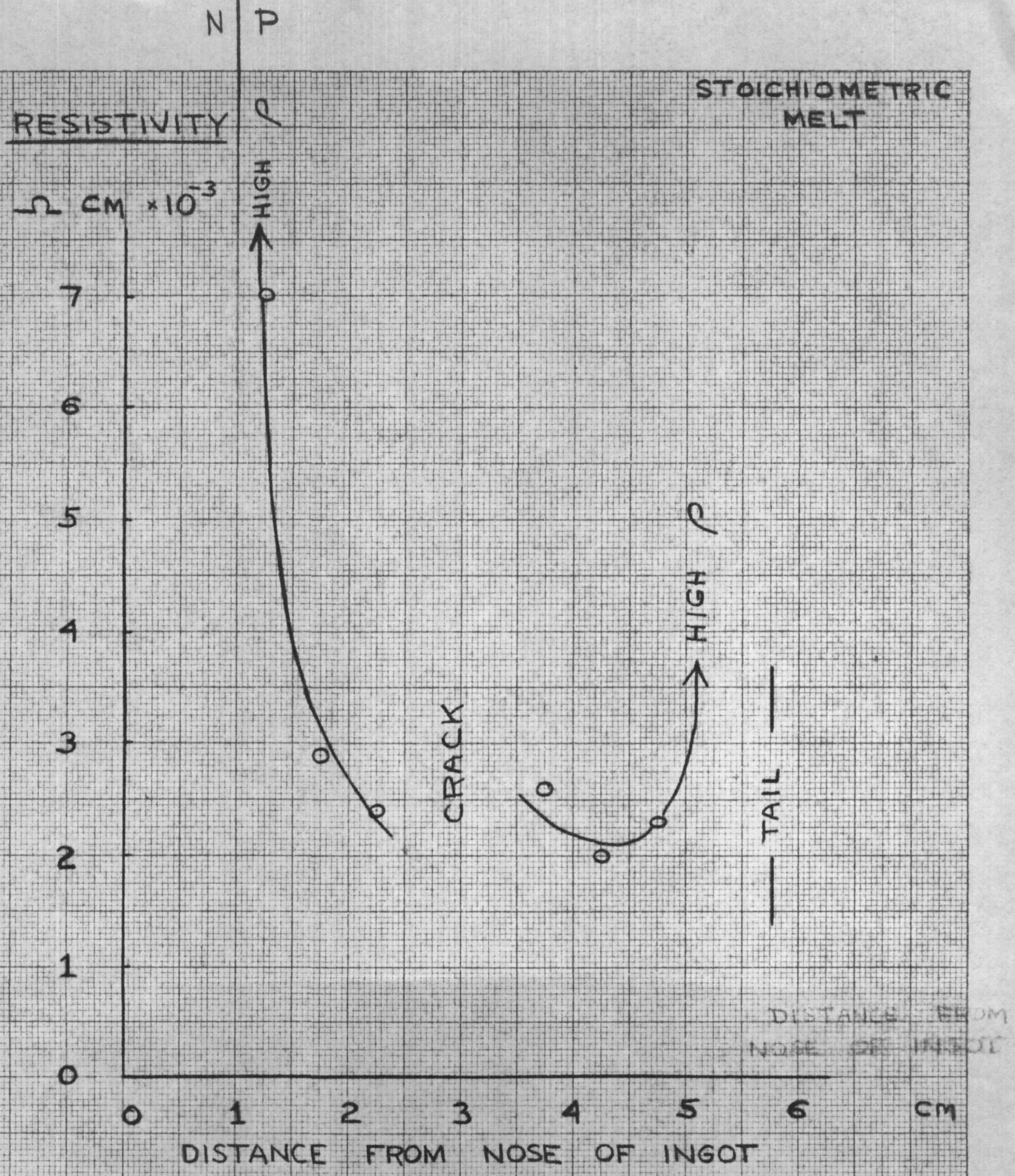

Figure 2. Electrical Resistivity Profile in Stoichiometric PbTe

Initial Melt Composition: 49.5% Pb, 495% Te, 1% As.

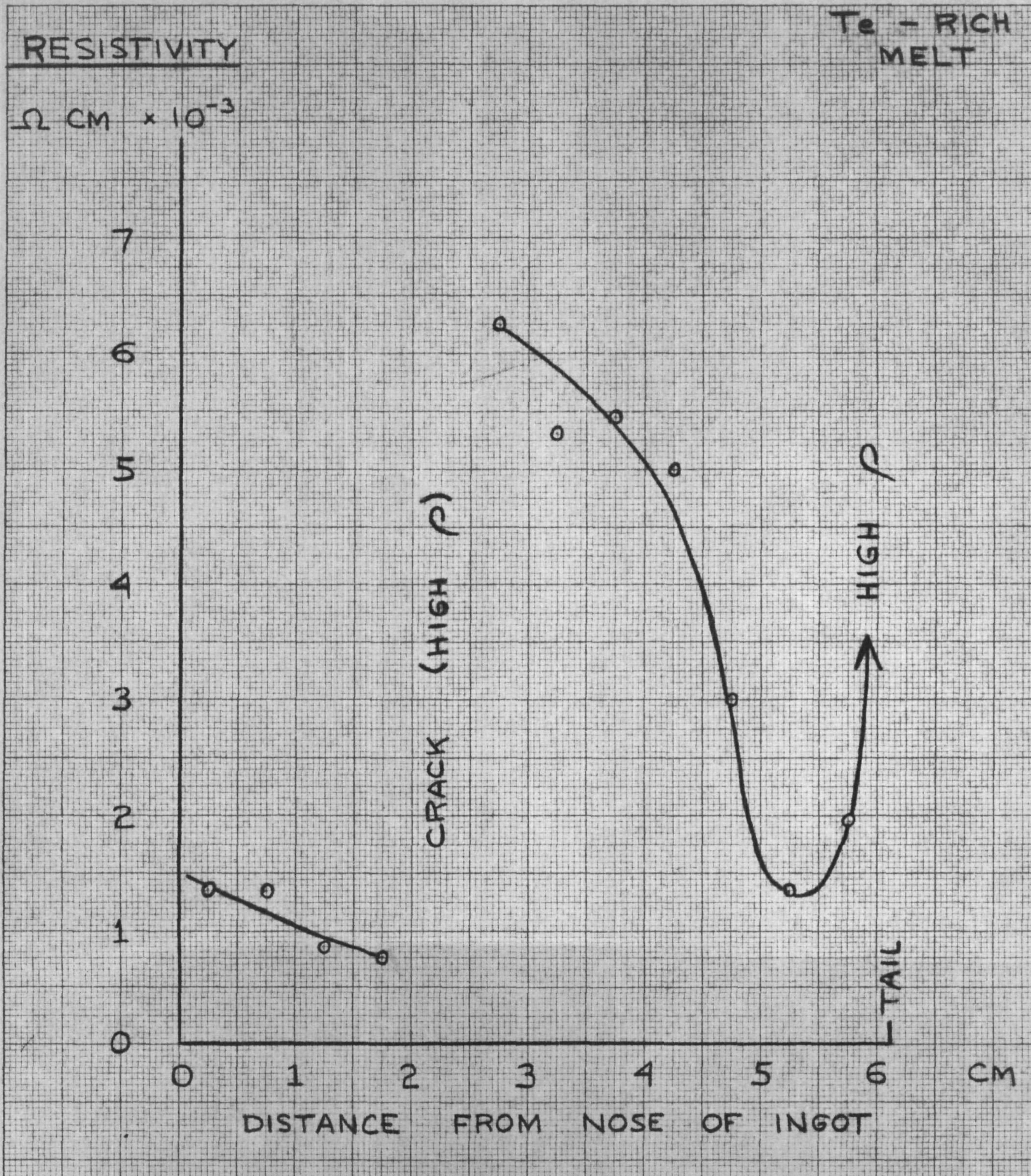

Figure 3. Electrical Resistivity Profile in Tellurium-Rich PbTe.

Initial Melt Composition: 49.35% Pb, 49.65% Te, 1% As.