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DEVELOPMENT OF TECHNIQUES FOR PREPARING
HOMOGENEOUS SINGLE CRYSTALS OF LEAD
TELLURIDE, LEAD SELENIDE, AND LEAD SULFIDE

J.F. Miller, et al

Battelle Memorial Institute
Columbus, Ohio

15 October 1965

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SEVENTEENTH QUARTERLY PROGRESS REPORT

on

DEVELOPMENT OF TECHNIQUES FOR
PREPARING HOMOGENEOUS SINGLE
CRYSTALS OF LEAD TELLURIDE, LEAD
SELENIDE, AND LEAD SULFIDE

to

MASSACHUSETTS INSTITUTE
OF TECHNOLOGY

October 15, 1965

by

J. W. Moody, J. F. Miller, R. C. Himes,
and H. L. Goering

Subcontract No. 212 of Prime
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July 15 to October 15, 1965

BATTELLE MEMORIAL INSTITUTE
505 King Avenue
Columbus, Ohio 43201

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December 22, 1965

Dr. A. J. Strauss
Assistant Group Leader
Division 8, Group 83
Lincoln Laboratory
Massachusetts Institute of
Technology
Lexington, Massachusetts 02173

Dear Dr. Strauss:

Enclosed are ten copies of the Seventeenth Quarterly Report on your project "Development of Techniques for Preparing Homogeneous Single Crystals of Lead Telluride, Lead Selenide, and Lead Sulfide". This report covers the period July 15 through October 15, 1965.

In accordance with the plans outlined in our letter proposal of May 6, 1965, we have resumed the study of the effects of impurities in PbTe. Work on the purification of PbTe by vacuum sublimation has been continued also.

Your comments and suggestions concerning this report will be welcomed.

Sincerely yours,



J. F. Miller, Associate Chief
Physical Chemistry Division

JFM:so
Enc. (10)

cc: See Distribution List

DEVELOPMENT OF TECHNIQUES FOR PREPARING HOMOGENEOUS SINGLE CRYSTALS OF LEAD TELLURIDE, LEAD SELENIDE, AND LEAD SULFIDE

by

J. W. Moody, J. F. Miller, R. C. Himes,
and H. L. Goering

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INTRODUCTION

This is the Seventeenth Quarterly Progress Report on the project. It covers the period July 15 through October 15, 1965.

In previous study on the project of the purification of PbTe by vacuum sublimation, it has been shown that sublimation is an effective means of reducing the concentration of certain impurities in PbTe and of preparing relatively low-carrier concentration, high-mobility crystals of PbTe. Some additional experiments on the process have been accomplished this quarter.

Some effort has been shifted to a study of the effects of impurities in PbTe. The effects of platinum and mercury are now under study and are discussed in this report.

SUMMARY

In the studies to date, PbTe with platinum has been found to produce low-carrier-concentration, high-mobility material. Certain platinum-doped samples exhibit the double crossover of the Hall coefficient in the temperature range 77-420°K. It is believed that the observed characteristics result from the interaction of platinum atoms and stoichiometric defects. Further consideration of the effects of platinum, along with those of other impurities, is planned.

Initial experiments indicate that doping PbTe with mercury produces high-carrier-concentration, low-mobility, p-type material.

A number of successive sublimations of n-type PbTe at 700°C was found to produce the low-mobility material similar to that previously obtained after three or four sublimations at 800°C. Heat treatment of the low-mobility samples in the vapor of lead-rich PbTe stock converted them to high-mobility material.

The electrical properties observed for the crystals at temperatures down to 77°K appear to be dominated by native defects and are strongly dependent upon the thermal history of the crystal. Electrical-property studies down to liquid-helium temperature are planned for the purpose of determination of the effects of foreign impurities.

Accepted for the Air Force
Franklin C. Hudson
Chief, Lincoln Laboratory Office

EXPERIMENTAL DETAILS AND DISCUSSION

Platinum as a Dopant in PbTe

In previous work (Seventh Quarterly Progress Report, April 15, 1963) a crystal (18761-98) of PbTe was grown at about 0.06 in./hr from a melt containing stoichiometric amounts of lead and tellurium plus 0.1 weight percent of platinum. Thermoelectric probing at about room temperature revealed that the first-to-freeze portion of the crystal was p-type, the last-to-freeze portion was n-type. The p-n junction was located at about the middle of the crystal. The Hall coefficients of samples taken from both the p- and n-type regions of the crystal exhibited double crossover when measured as a function of temperature.

Recently a second platinum-doped crystal was prepared. This crystal (21321-85) was grown at about 0.05 in./hr from a melt containing about 50.012 atomic percent tellurium, 49.988 atomic percent lead (near the maximum melting composition in the Pb-Te system), plus about 0.1 weight percent platinum. The entire crystal appeared to be n-type when probed at room temperature with the thermoelectric probe. A four-probe resistivity profile of the crystal is shown in Figure 1. For comparison, the four-probe resistivity profile on an undoped crystal is also shown in Figure 1. The undoped crystal, 21321-84, was grown at about 0.5 in./hr from a melt of the congruent melting composition. It was p-type and of relatively uniform resistivity over its entire length as expected. In contrast, the room-temperature resistivity of the Pt-doped crystal varied considerably over the length of the crystal and was a maximum near the center of the crystal.

The Hall coefficients of several samples from the platinum-doped crystals are plotted as a function of reciprocal temperature in Figure 2. Sample 18761-98-N2 was from the portion of Crystal 18761-98 which was n-type at room temperature and at 77°K; Samples 21321-85-1 and 21321-82-2 were from the front and rear, respectively, of Crystal 21321-85. The Hall coefficient of 21321-85-1 which was positive at the terminal temperatures exhibited double crossover behavior, whereas the Hall coefficient of 21321-85-2 was negative over the temperature range covered (77°K to about 420°K).

The resistivities of the platinum-doped samples are plotted as a function of reciprocal temperature in Figure 3. Although the characteristics are not fully apparent, the top two curves give evidence of the typical behavior of resistivity through the crossover region in which, as was shown for various crystals in the Twelfth Quarterly Report, September, 1964, maxima occur roughly at the crossover temperatures.

Two platinum-doped samples were annealed at elevated temperatures in the vapor of lead-rich PbTe stock. These samples were taken from the p-type region of Crystal 18761-98. The effect of the heat treatment on the properties of the samples is shown by the data in Table 1, which lists the properties of the samples at 77°K. It will be noted that the electron concentrations in the samples were increased by the heat treatment. However, the carrier concentrations of the annealed samples were considerably less than would be expected for undoped samples heat treated under the same conditions, i.e., 2×10^{18} and $2-4 \times 10^{17}$ per cm^3 at 800 and 850°C, respectively. Thus, insofar as the free-electron concentration and solubility of lead correspond, platinum appears to reduce the effective solubility of lead in PbTe. After heat treatment, the Hall coefficients of the samples did not exhibit double-crossover behavior, but were negative over the entire temperature range covered.

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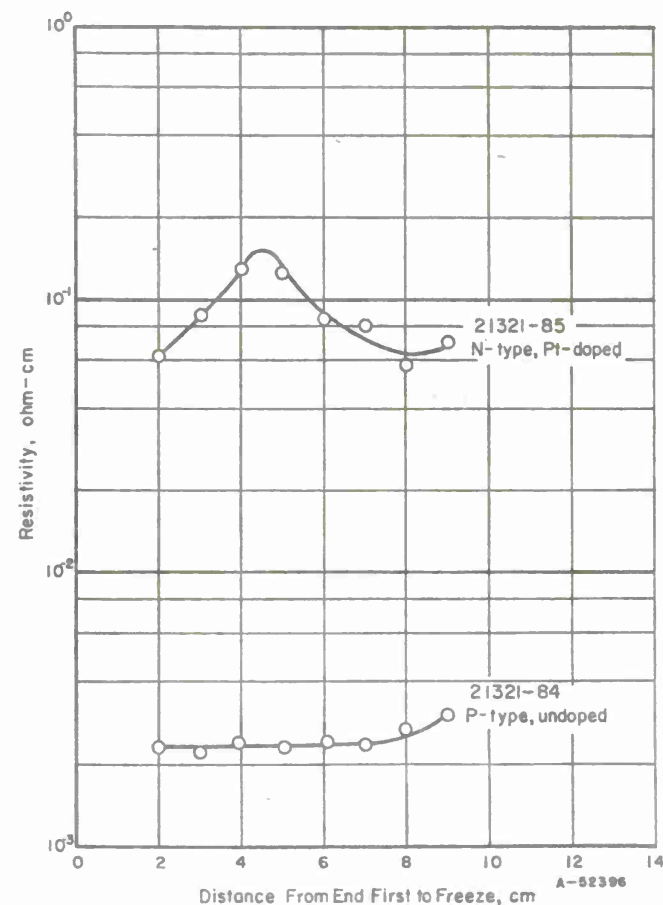


FIGURE 1. FOUR-PROBE RESISTIVITY PROFILE AT ROOM TEMPERATURE OF BRIDGMAN-GROWN PbTe CRYSTALS

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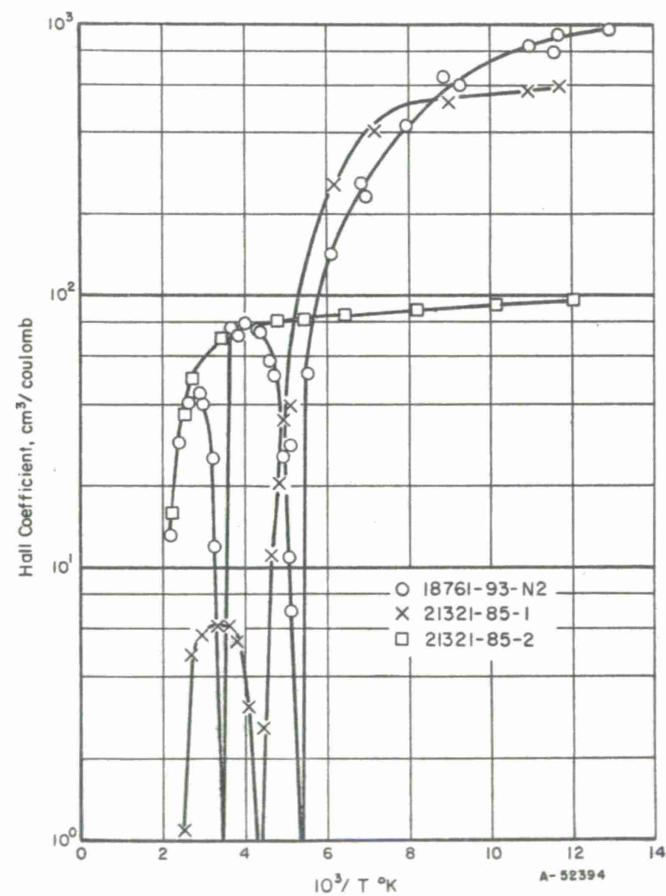


FIGURE 2. HALL COEFFICIENT AS A FUNCTION OF RECIPROCAL TEMPERATURE FOR VARIOUS AS-GROWN PT-DOPED CRYSTALS OF PbTe

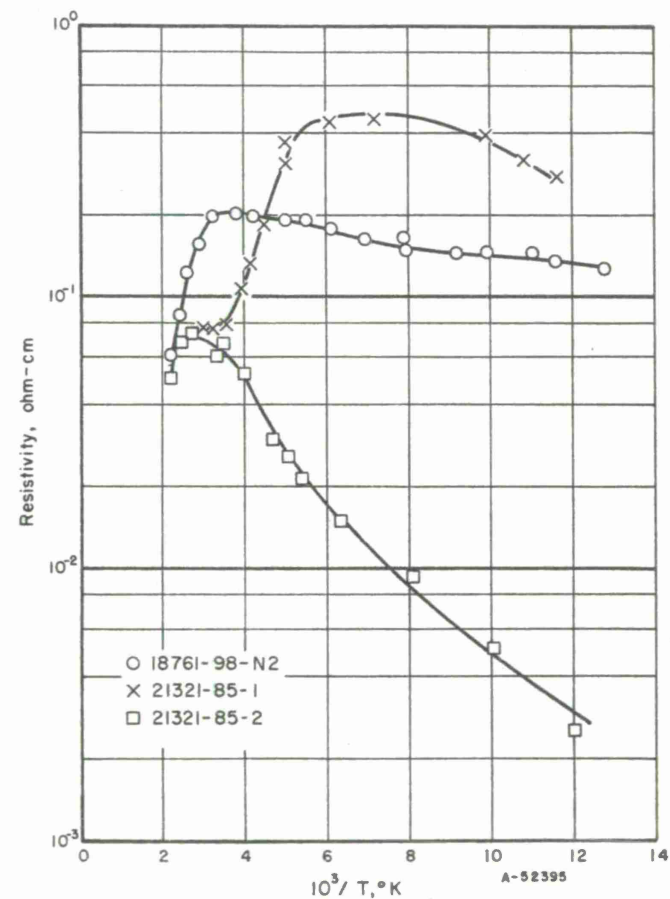


FIGURE 3. RESISTIVITY AS A FUNCTION OF RECIPROCAL TEMPERATURE FOR VARIOUS AS-GROWN PT-DOPED CRYSTALS OF PbTe

TABLE 1. EFFECT OF HEAT TREATMENT ON PROPERTIES (AT 77°K) OF PLATINUM-DOPED PbTe

Sample	Treatment	Hall Coefficient, cm ³ /coulomb	Resistivity, ohm-cm	Mobility, cm ² /volt-sec	Carrier Concentration, cm ⁻³
18761-98-P2	As prepared	-1270	2.36×10^{-1}	5.4×10^3	4.8×10^{15}
18761-98-P2	800°C anneal	-6.2	2.00×10^{-4}	3.1×10^4	1.0×10^{18}
18761-98-P1	855°C anneal	-103	3.32×10^{-3}	3.1×10^4	6.1×10^{16}

The mobilities at 77°K of various platinum-doped samples are plotted as a function of carrier concentration (at 77°K) in Figure 4. The open circles are for samples from "as-prepared" platinum-doped crystals; the solid circles are for platinum-doped samples which had been heat treated in the vapor of lead-rich PbTe stock. With the exception of 21321-85-1, the carrier concentration-mobility data of these doped samples are roughly comparable with, or mobilities are slightly higher than, those of undoped PbTe. (The "normal" curve exhibits a maximum in mobility at about $2-4 \times 10^{17}$ electrons/cm³.) Thus, a single type of impurity center appears to dominate the conduction process at 77°K in all samples except 21321-85-1, which is apparently compensated at this temperature.

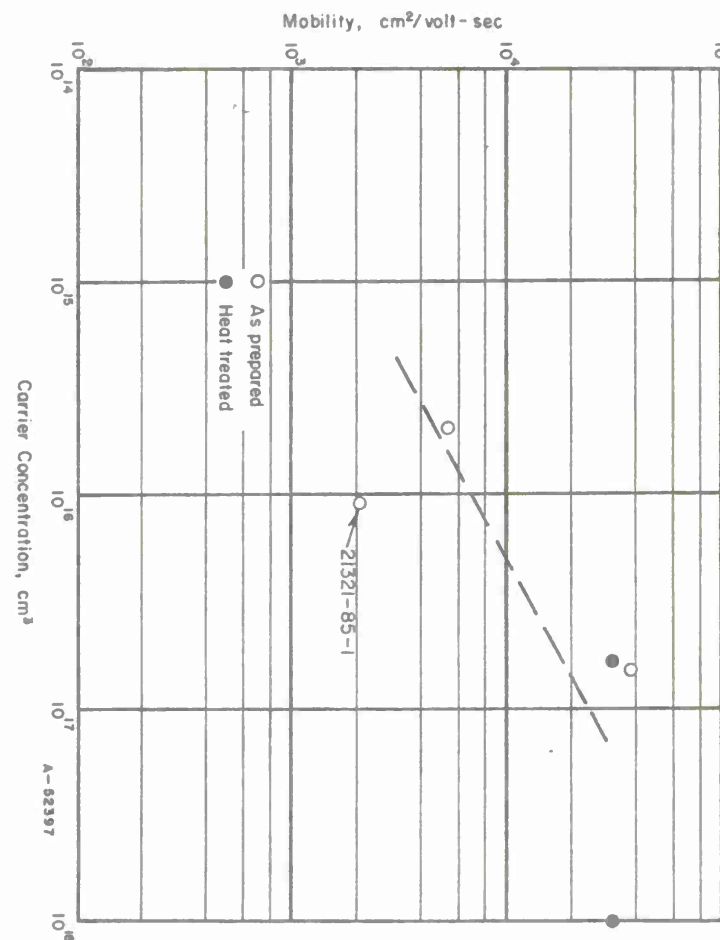
Crystals of PbTe, which are grown from undoped stoichiometric or tellurium-rich melts, are p-type at room temperature (except perhaps for the very last-to-freeze portion). That Crystals 18761-98 and 21321-85 which were cast from platinum-doped melts were largely or entirely n-type indicates that platinum is a donor in PbTe. This indication is supported by the observation that platinum appears to reduce the effective solubility of lead in PbTe. Such behavior is opposite to that of copper which increases the effective solubility of lead in PbTe and is believed to be an acceptor in PbTe. However, a simple donor model for platinum does not account for the low-carrier concentration of "as prepared" crystals, or the double-crossover behavior observed in certain samples. It is likely that platinum atoms react with stoichiometric defects to produce the observed effects. Effort will be made to develop a model to account for the properties of platinum-doped PbTe. Selected crystals are to be analyzed to determine the concentrations of platinum present in the crystals.

It is worthy of note that doping with platinum appears to be an effective means of preparing PbTe with low n-type carrier concentrations ($<10^{16}$ cm⁻³) with high electron mobilities for those carrier concentrations.

Mercury as a Dopant in PbTe

In this quarter, the electrical properties of samples from mercury-doped crystals prepared previously (Seventh Quarterly Progress Report, April 15, 1963) were measured as a function of temperature. The crystals, 19733-8 and 19733-9, were cast from tellurium-rich melts and were p-type except for caps of the very last-to-freeze material. Carrier concentrations of samples from both as-grown crystals were above 10^{18} holes/cm³, from liquid-nitrogen to room temperature but were not "well behaved" with temperature. The Hall coefficient of one sample exhibited a maximum at about 125°K, while

FIGURE 4. CHARGE CARRIER MOBILITY VERSUS CARRIER CONCENTRATION AT 77°K FOR Pt-DOPED PbTe CRYSTALS



the Hall coefficient of the second was constant from 77°K to about 200°K, then increased slowly with increasing temperature; mobilities were low throughout this range.

Since the study of the effects of mercury doping has just been initiated, the data available are limited. Further discussion of the effects of mercury in PbTe will be deferred until additional data are collected.

Vacuum Sublimation of PbTe

It is recalled that the charge-carrier mobilities of crystals grown from PbTe which has been vacuum sublimed three or four times at 800°C (starting with an n-type charge as described in the Sixteenth Quarterly Report, July, 1965) are abnormally low, whereas relatively high-mobility crystals are obtained from the material after one or two sublimations. The crystals of PbTe which had been vacuum sublimed at 800°C have been annealed at 822°C in the vapor of lead-rich PbTe stock for 48 hours. The crystals were then quenched. The electrical properties at 77°K of the crystals, before and after the heat treatment, are listed in Table 2. The most significant effect of the heat

TABLE 2. EFFECT OF HEAT TREATMENT ON THE PROPERTIES
(AT 77°K) OF VACUUM SUBLIMED PbTe(a)

	Sample Number		
	21321-51-1 Sublimed Once	21321-52A Sublimed Three Times	21321-66-1 Sublimed Four Times
<u>Before Anneal</u>			
Resistivity, ohm-cm	1.64×10^{-4}	2.49×10^{-3}	1.39×10^{-4}
Hall Coefficient, cm ³ /coulomb	-5.3	-3.9	-3.3
Carrier Concentration, cm ⁻³	1.2×10^{18}	1.6×10^{18}	1.9×10^{18}
Mobility, cm ² /volt-sec	3.2×10^4	1.6×10^3	1.8×10^4
<u>After Anneal(b)</u>			
Resistivity, ohm-cm	1.10×10^{-4}	1.18×10^{-4}	1.12×10^{-4}
Hall Coefficient, cm ³ /coulomb	-2.9	-3.3	-2.9
Carrier Concentration, cm ⁻³	2.1×10^{18}	1.9×10^{18}	2.1×10^{18}
Mobility, cm ² /volt-sec	2.7×10^4	2.8×10^4	2.6×10^4

(a) Quenched n-type initial charge of PbTe.

(b) At 822°C in the vapor of Pb + PbTe for 48 hours, followed by quenching to room temperature.

treatment is the increase of the charge-carrier mobility in Crystals 21321-52A and 21321-66-1. Before the anneal, the carrier-concentration-mobility data suggest that these samples are "compensated". After the anneal, the carrier mobilities for the crystals are as high as those expected for essentially uncompensated specimens at the measured carrier concentrations which, it can be noted, increased slightly for these crystals on heat treatment. For Crystal 21321-51-1 the carrier concentration increased and the mobility decreased slightly as a result of the heat treatment. After the anneal, the properties of all three samples are nearly identical, indicating that the properties observed at temperatures down to 77°K are determined primarily by the final heat-treatment conditions. The effect of the sublimations, if any, is not discernible now.

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An n-type charge of PbTe was distilled four times at 700°C. A crystal grown at 700°C from the final sublimate had a carrier concentration of 1.1×10^{18} electrons/cm³ and a mobility of 2.4×10^4 cm²/volt-sec at 77°K. A mobility greater than 3.0×10^4 cm²/volt-sec can be expected for such a carrier concentration. Thus, successive sublimations at 700°C finally lead to low-mobility material similar to that obtained after a number of sublimations at 800°C. As has been suggested previously, the properties observed after a number of successive sublimations may be due to the interactions of native stoichiometric defects. In addition, as shown above, heat treatment in the vapor of lead-rich PbTe stock restores the high mobility, indicating that the low mobility observed at temperatures down to 77°K after a number of sublimations is due to an intrinsic property of PbTe rather than to foreign impurities.

Electrical-property measurements on selected vacuum-sublimed specimens at temperatures down to the liquid-helium temperature are planned to look for effects of residual foreign-impurity concentrations.

FUTURE PLANS

Plans for the future call for a continuation of the study of the effects of impurities in PbTe. It is expected that the work will be concerned primarily with mercury. Additional mercury-doped crystals will be prepared and samples will be heat treated. Consideration of the effects of platinum doping will be continued also to develop a model to account for the properties of platinum-doped samples. Some additional investigation of electrical properties of vacuum-sublimed materials at low temperatures is planned also to study the effects of foreign impurities.

Data upon which this report is based can be found in Battelle Laboratory Record Book No. 21321, pp 75-89.

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