J. Phys. Chem. Solids Pergamon Press 1959. Vol. 9. pp. 325–329. Printed in Great Britain.

PREPARATION AND PROPERTIES OF HgTe AND MIXED CRYSTALS OF HgTe–CdTe

W. D. LAWSON, S. NIELSEN, E. H. PUTLEY and A. S. YOUNG

Royal Radar Establishment, Malvern, England

(*Received* 16 *October* 1958)

Abstract—The elements mercury, cadmium, and tellurium have been purified, and crystals of the compounds CdTe and HgTe, and of the mixed compounds CdTe–HgTe have been prepared. X-ray and cooling-curve data have established that CdTe and HgTe mix in all proportions to give single-phase crystals. Hall-coefficient and conductivity measurements show that HgTe is a semiconductor with a very low activation energy ($\sim 0{\cdot}01$ eV) and a high mobility ratio (~ 100). HgTe is opaque to infrared radiation out to a wavelength of 38 μ, but the mixed crystals show absorption edges which vary in position with composition from $0{\cdot}8\ \mu$ in pure CdTe to 13 μ in crystals containing 90 per cent HgTe. Photoconductivity has been observed in filamentary detectors made from the mixed crystals.

1. PREPARATION

THE compounds HgTe and CdTe were prepared by direct synthesis from the elements *in vacuo*, in sealed silica crucibles. CdTe presented no problem, but the formation, subsequent zone melting, and crystal growth of HgTe had to be carried out in specially prepared thick-walled silica crucibles because of the high vapour pressure of free mercury (22 atm. at 600°C). We used crucibles with an internal diameter of 10 mm and a wall thickness of 3 mm; these were capable of withstanding an internal pressure of about 150 atm.

Preparation involved the following stages: (*a*) purification of the elements, (*b*) synthesis of the compounds HgTe and CdTe, (*c*) zone purification and crystal growth of these two compounds, and (*d*) preparation of mixed crystals from the two compounds.

Mercury was purified by shaking to an emulsion for several minutes with dilute nitric acid (this removes base-metal impurities), filtering and distilling slowly in a quartz apparatus *in vacuo*. It is essential to avoid breaking the surface of the mercury during distillation, by boiling or "bumping", as this causes droplets of the undistilled mercury to be thrown over. It was found, using radiotracers, that most impurities were reduced in concentration to well below 0·1 p.p.m. by this process.* It is worth mentioning in this connection that as little as 0·1 p.p.m. of metals such as sodium lithium, lead, tin, indium and zinc in mercury produce a visible surface scum.

Cadmium was purified by repeated distillation *in vacuo* or in a low-pressure stream of hydrogen (from a palladium leak) as indicated in Fig. 1a. Hydrogen is especially advantageous, as it reduces

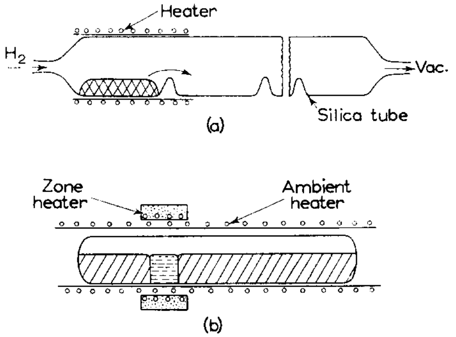

FIG. 1. (*a*) Apparatus for distilling cadmium and tellurium. (*b*) Apparatus for zone melting and growing crystals of the compounds.

---

* We are indebted to Dr. F. M. REYNOLDS of the National Chemical Laboratory for suggesting this process and for checking its efficiency with radiotracers.

any oxides present and thus prevents the ingots from sticking to the silica crucibles. Tellurium was also processed in this way and was in addition zone-refined *in vacuo* in sealed silica crucibles. The efficiency of the distillation and zone-melting processes was checked by spectrographic methods, using doped specimens to bring the initial impurity concentrations well within the limits of detection of the spectrograph. The purity of our tellurium was also checked by Hall-coefficient measurements, and we obtained material with an extrinsic Hall coefficient of $+40{,}000\ \text{cm}^3/\text{C}$, which corresponds to a carrier concentration of 2×10^{14} positive holes per cm^3. It was discovered during this investigation that the Hall coefficient of a specimen of tellurium is influenced very markedly by the physical nature of its surface, and we found it essential to etch the specimens very carefully in order to achieve consistent results. The Hall coefficient can be reduced by a factor of over a hundred by abrasion or roughening of the surface; even polishing produces a marked reduction.

The compounds CdTe and HgTe were prepared by introducing weighed amounts of the elements into the appropriate silica crucible, which was subsequently pumped to a residual air pressure of 10^{-6} mmHg and sealed off. The crucible was then heated slowly to a temperature just above the melting point of the compound in a furnace which was rocked gently to and fro.

Both compounds were zone-refined in an apparatus of the type shown in Fig. 1b, in which the solid parts of the ingot could be maintained at a uniformly high temperature to prevent undue transfer of material from the molten zone by evaporation. Because of the high vapour pressure of molten HgTe, an ambient temperature within 50°C of the melting point was necessary. A zone rate of 5 cm/hr was used. Single crystals were grown in the same apparatus using a crucible with a tapered end and a zone rate of 1 cm/hr.

The mixed crystals of HgTe–CdTe were prepared by melting together the appropriate weights of the purified compounds *in vacuo*, in sealed, thick-walled, silica crucibles. Preparation directly from the elements usually resulted in explosions, which were probably caused by very high pressures from local pockets of uncombined mercury. Single crystals of the mixtures were grown in the same way as the compounds.

HgTe and CdTe both have the zinc-blende structure with lattice parameters,* i.e. the edge dimension of the unit cube, 6·460 and 6·480Å, respectively, a difference of 0·31 per cent. X-ray examination of the mixed crystals indicated that they were single phase over the whole range from pure CdTe to pure HgTe, and this was confirmed by classical cooling-curve methods. The melting point of CdTe was found to be 1106° C and that HgTe 600°C. The variation of melting point with respect to composition of the mixed compounds was almost linear between these two values.

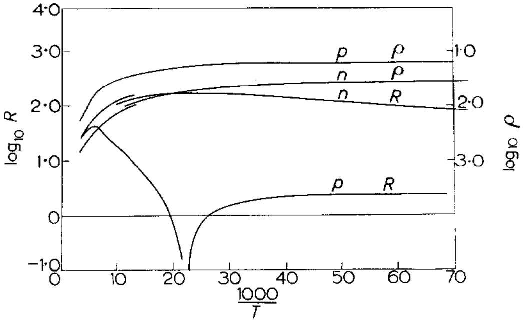

FIG. 2. Variation with temperature of Hall coefficient R and resistivity ρ of one n-type and one p-type crystal of HgTe (R in cm^3/C. ρ in Ω-cm).

2. RESULTS OF ELECTRICAL MEASUREMENTS

Fig. 2 shows Hall-coefficient and resistivity values between 14 and 290°K for two specimens HgTe, one n-type, the other p-type. From the Hall curve for the p-type crystal, the mobility ratio c can be calculated, using the relation

$$\left|\frac{R_{\text{ext}}}{R_{\max}}\right| = \frac{4c}{(c-1)^2}.$$

This gives $\mu_e/\mu_h = c = 70$. Also $R_{\max}/R_i = (1+c)/4c$ at the temperature of $R_{\max}$, 174°K. This gives R_i, and hence the intrinsic carrier concentration $N_i = 6{\cdot}4\times 10^{17}$ per cm^3 at 174°K. By assuming that c does not vary with temperature, values of N_i at other temperatures, e.g. at 44·5°K where R is zero, can be obtained. The values at 284 and at 116°K were obtained by solving the general expression for R, again using the same

---

* We are indebted to Miss A. E. RENNIE for the X-ray measurements.

value of c. The values of N_i are given in Table 1. The activation energy can now be deduced and a value of $\sim 0{\cdot}01$ eV is obtained.

Table 1. *Intrinsic carrier concentration in HgTe*

T(°K)	284	174	116	44·5
$N_i(\div 10^{17})$	6·8	6·4	2·3	0·46

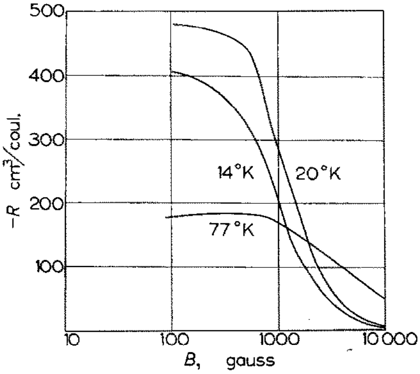

Fig. 3. P-type crystal of HgTe. Variation of Hall coefficient with magnetic field at 14, 20, and 77°K.

Fig. 3 shows the variation of Hall coefficient with magnetic field in the n-type crystal of HgTe. An analysis of this,* following the method used for InSb,(1) yields the following results at 77°K:

$$c = 120;\ N_i = 0{\cdot}612\times 10^{17}\ \text{per cm}^3;\ \mu_e = 6120;\ \mu_h = 51.$$

It will be seen that the value of N_i obtained by this analysis agrees with the values given in Table 1.

The results of Hall-coefficient and conductivity measurements on one of the mixed crystals, an n-type specimen containing 90 mol. per cent mercury, are given in Fig. 4. Similar results were obtained from other crystals containing a high percentage of mercury. The results have not been analysed in detail, but mobility appears to follow a T^{-2} law approximately (values from 1·7 to 2·2 were obtained).

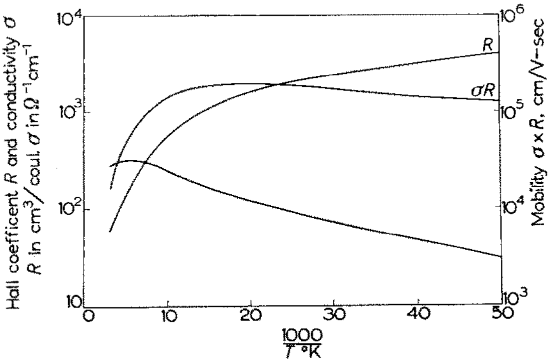

Fig. 4. Variation with temperature of Hall coefficient R, conductivity σ, and Hall mobility $R\times\sigma$, of a mixed crystal of composition $Hg_{0{\cdot}9}Cd_{0{\cdot}1}Te$.

Table 2 gives spot measurements at 77 and at 300°K of R, σ and $R\times\sigma$ for some of the mixed

Table 2. *Hall coefficient, conductivity, and Hall mobility of mixed crystals of CdTe–HgTe at* 300 *and* 77°*K*

Composition (mol.–% Hg)	Conductivity $\sigma(\Omega^{-1}\ \text{cm}^{-1})$		Hall coeff. R(cm³/C)		$R\times\sigma$ (cm²/V-sec)	
	300°K	77°K	300°K	77°K	300°K	77°K
100	790	109	24	215	19,000	23,400
90(1)	314	261	72	1030	22,600	269,000
90(2)	320	149	71·4	1000	22,800	149,000
84	130	30·4	112	869	14,560	26,400
75	32	9·5	101·5	330	3,250	3,140
50	4·5	4·8	194	37·6	870	180
40	1·5	1·1	52	190	78	209

---

* Carried out by Dr. D. J. Howarth.

crystals, all *n*-type specimens. The main feature is that some very high values of Hall mobility were obtained in some of the specimens. These are not necessarily the maximum values obtainable; further work on the preparation of more perfect crystals may yield even higher electron mobilities.

3. OPTICAL RESULTS

Crystals of pure HgTe were opaque to infrared radiation out to a wavelength of 38μ, the limit of our apparatus, and at temperatures down to 4°K. This indicates that the activation energy is lower than 0·03 eV, in line with the electrical results. Crystals of the mixed compounds were, however, found to be transparent at lower wavelengths, and the results of measurements taken at room temperature are given in Fig. 5. The results are presented as curves of $\log_{10} I_0/I$ against wavelength in microns, where I_0 is the incident and I the transmitted energy; no attempt has been made to calculate absorption coefficients as the refractive index, and hence the reflection loss, is not known. It will be seen that the absorption edge moves from 0·8μ in pure CdTe to 13μ in the mixed crystals as the ratio of mercury increases to about 90 per cent.

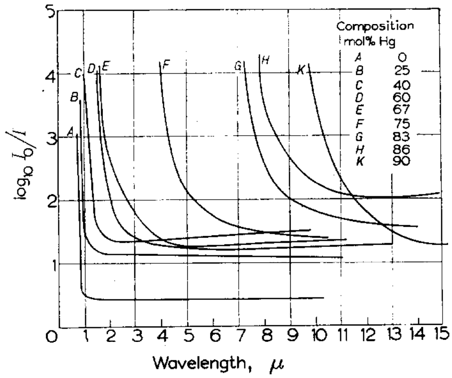

FIG. 5. Room-temperature absorption curves of mixed crystals of HgTe–CdTe. (I_0 = incident energy; I = transmitted energy).

The free-carrier absorption beyond the edge tends to increase, and the absorption edges themselves become less steep, as the position of the edge moves to longer wavelengths, thus making the estimation of the exact position of the edge by inspection of the curves progressively more difficult. However, estimates were made by extrapolating those regions of the curves where free-carrier absorption predominates backwards through the absorption edges and subtracting this component, which also includes reflection loss, from the observed total values. The remainder is proportional to the absorption coefficient for electronic transitions across the forbidden gap, and plots of the square root of this quantity against energy E eV, where $E = 1{\cdot}24/\lambda$, give approximately straight lines. The intersects of these on the E axis were taken as the activation energies for the particular crystals, and the corresponding values of λ as their absorption edges.

Fig. 6 shows how the absorption edge calculated in this way varies with composition. The curve cannot be drawn with sufficient certainty at the mercury-rich end to enable an accurate value of the activation energy of pure HgTe to be obtained by extrapolation. However, it is evident from Fig. 6 that this series of compounds can provide, by suitable choice of composition, a range of infrared filters and detectors to operate anywhere in the region from 0·8μ to at least 15μ and, probably to much longer wavelengths.

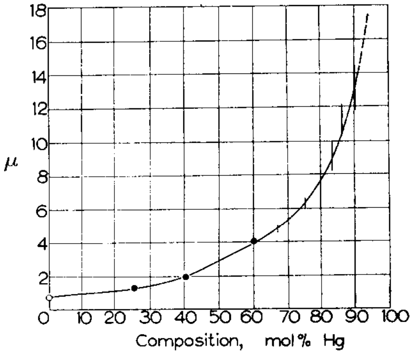

FIG. 6. Mixed crystals HgTe–CdTe. Variation of estimated position of absorption edge with composition.

4. PHOTOCONDUCTIVITY

Photoconductivity has been observed in thin filamentary detectors made from these crystals. The filaments were made by polishing and etching thin slices of the crystals, and some of the results are shown in Figs. 7 and 8. Fig. 7 shows the response curve of a crystal containing 86 per cent HgTe, and also shows that the limit of response moves to longer wavelengths on cooling. At the peak of the response the minimum detectable energy is about 2×10^{-8} W/cycle normalized to 10 mm^2 area. Fig. 8 gives some results for a crystal containing about 90 per cent HgTe. A measurable photoconductive signal was observed out to 13μ with the detector at room temperature; at longer wavelengths the signal was lost in noise. A P.E.M. signal was also observed, again with the detector at room temperature, as well as a photovoltaic signal which probably originated from a *p–n* junction in the crystal, near an electrode.

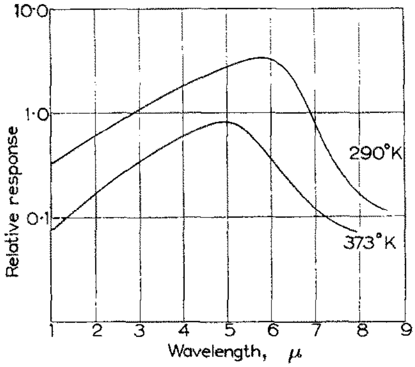

FIG. 7. Photoconductive response of a mixed crystal $\mathrm{Hg_{0\cdot86}Cd_{0\cdot14}Te}$, at 290 and 373°K.

The sensitivity at longer wavelengths of these detectors, when fully developed, may well be higher than that of impurity-doped silicon and germanium detectors; the sensitivity of a CdTe–HgTe detector depends on an intrinsic activation energy, so that its absorption efficiency should be much higher than that of a germanium or silicon impurity detector where the density of absorbing centres (impurities) may be limited.

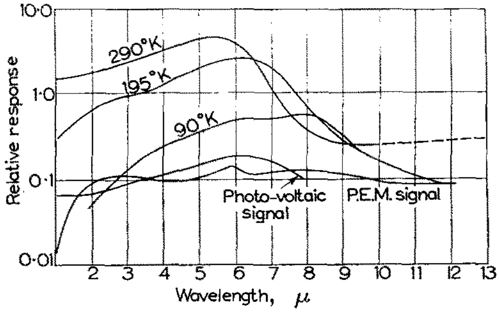

FIG. 8. Photoconductive response at 90, 195 and 290°K of a mixed crystal $\mathrm{Hg_{0\cdot9}Cd_{0\cdot1}Te}$. Photovoltaic and P.E.M. signals measured at 290°K.

Acknowledgements—The authors would like to thank G. G. STEEL, R. A. CLAY, R. J. HERITAGE and A. A. BROOKER for assistance with the preparation of specimens and measurements. The paper is published by permission of the Controller, H.M. Stationery Office.

REFERENCE

1. HOWARTH D. J., JONES R. H., and PUTLEY E. H., *Proc. Phys. Soc.* **B70**, 124 (1957).