

Induced defects in sintered lead telluride

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The effect of the pressing and sintering processes on some typical properties (carrier mobility and Hall effect) is analysed. In order to do this, samples obtained from powdered and pressed materials were submitted to a slow sintering process. During and after the thermal treatment, the samples were examined using both transport measurements and a scanning electron microscope in order to evaluate the sintering process. Thus some of the defects which influence electrical property variations have been seen.

1. Introduction

Lead telluride, a thermoelectric material having the highest figure-of-merit near 400°C, is used in very reliable self-contained energy conversion systems. It crystallizes in an NaCl-type cubic structure. This structure possesses anisotropy of its transport properties, and therefore the use of monocrystals as thermoelectric converters does not appear to be necessary [1]. On the other hand, pressed polycrystal compounds, which for thermoelectrical purposes are economically more advantageous, can have physical properties which are very different from those of monocrystals, as seen in the preparation of germanium-silicon thermoelectric elements [2].

In this work we have synthesized stoichiometric, Ag₂Te- and PbBr₂-doped PbTe samples and then after powdering and pressing, they were submitted to a slow sintering process. The following studies were then carried out on these samples.

(a) A scanning electron microscopy study was performed in order to obtain information on the characteristic parameters of powdered and pressed samples (surface area of monocrystal fragments per cm³, volumetric fraction of the pores) and in order to evaluate the development of the sintering process.

(b) A comparative study of the starting material transport properties (electrical conductivity and Hall constant) and of those induced properties in

the powdered and pressed samples was undertaken. In order to obtain some information about the nature of the defects primarily responsible for the electrical property variations, a study of the influence of annealing at 400°C on these properties was carried out at different annealing times. 400°C is the upper temperature limit since beyond this point undesirable side effects come into play. In fact a higher temperature which is useful for improving the sintering state also induces evaporation processes which alter the chemical composition of the matrix giving ambiguous results.

2. Experimental details

The starting elements were 99.999% pure and were further oxygen purified by melting in hydrogen flux. In the case of doped lead telluride, highly purified Ag₂Te and PbBr₂ were added to the starting elements which had been purified and weighed according to the 1:1 stoichiometric ratio. A direct synthesis of the elements was then carried out.

Stoichiometric PbTe and Ag₂Te-doped PbTe monocrystals were grown using the Bridgman method at the rate of 0.5 cm h⁻¹ and a thermal gradient of 20°C cm⁻¹. The samples used for powdering were cut from the central part of monocrystalline ingots. The silver content was determined by the method described in [3] and by the X-ray microanalysis.

TABLE I Summary of the results. Symbols N_A , l , f_v : see text. (a) as-grown monocrystal; (a') polycrystalline; (b) as (a) or (a') after powdering and pressing; (c) as (b) after 54 h sintering; (d) as (c) after 310 h sintering. Values are undeterminable because of the low statistics

Sample composition	Treatment	$N_A(10^4 \text{ cm}^{-2})$	$l(\mu\text{m})$	$S_v(10^4 \text{ cm}^2/\text{cm}^{-3})$	f_v	$\sigma(\Omega^{-1} \text{ cm}^{-1})$ (100° C)	Figure
Stoichiometric PbTe	a	—	—	—	—	5×10^4	
	b	5	26 ± 5	0.16	—	0.2	
	c	5	25 ± 5	0.14	0.15	20	
	d	4	29 ± 5	0.06	0.13	$60 \div 70$	2
PbTe doped with 0.22 mol % Ag_2Te	a	—	—	—	—	10^4	
	b	2	50 ± 5	—	—	13	
	c	2	50 ± 5	—	0.23	20	
	d	2	50 ± 5	—	0.23	30	
PbTe doped with 0.055 mol % Ag_2Te	a	—	—	—	—	10^4	
	b	1	80 ± 5	—	—	10	
	c	1	80 ± 5	—	0.25	13	1
	d	1	80 ± 5	—	0.30	20	
PbTe doped with 0.025 mol % PbBr_2 (p-type)	a'	—	—	—	—	9.5×10^3	
	b	—	—	—	—	0.4	
	c	—	—	—	—	9	
	d	—	—	—	0.24	28	
PbTe doped with 0.05 mol % PbBr_2 (n-type)	a'	—	—	—	—	7.5×10^3	
	b	1	85 ± 5	—	—	2.5	
	c	1	85 ± 5	0.03	0.15	15	
	d	1	90 ± 5	0.04	0.10	70	3
PbTe doped with 0.1 mol % PbBr_2	a'	—	—	—	—	2.2×10^4	
	b	—	—	—	—	7	
	c	—	—	—	0.25	20	
	d	—	—	—	0.26	85	

PbTe polycrystals doped with PbBr_2 were obtained from the melt by direct synthesis.

All melts and annealing were carried out in quartz tubes and in a neutral (Ar or N_2) or reducing (H_2) atmosphere. The sintered materials were obtained by powdering and crushing in agate mortars at 200 g cm^{-2} .

Electrical conductivity (σ) and the Hall constant (R_H) were detected simultaneously using cross modulation of both the sample current (at a frequency of 84 Hz) and the magnetic field (at a frequency of 36 Hz). The Hall voltage was measured at the sum of the two frequencies (120 Hz).

3. Results and discussion

3.1. Scanning electron microscopy examinations (SEM)

Scanning electron microscopy (SEM) was used to observe the surfaces of freshly fractured samples listed below: stoichiometric PbTe, PbTe doped with 0.022 mol % Ag_2Te , 0.055 mol % Ag_2Te , 0.025 mol % PbBr_2 , 0.05 mol % PbBr_2 and 0.1 mol % of PbBr_2 .

The following measurements were made on the

surfaces: the number of monocrystal fragments per cm (N_A); the average dimension of monocrystal fragments (l); the surface area of monocrystal fragments per cm^3 (S_v); and the fraction of the pores per volume unit (f_v). N_A and l characterize the degree of crushing; S_v characterizes the degree of compacting and densification; f_v characterizes the development of the sintering process in terms of reduction of porosity between matrix and monocrystal fragments and between one fragment and another. A summary of the results is shown in Table I.

The material, after having been treated for 58 h, appeared to have undergone considerable changes compared with its initial state. A further increase in the sintering process versus a lengthening of annealing time is not evident except for that material which was doped with 0.025 and 0.05 mol % PbBr_2 . Typical microstructures are shown in Figs. 1 to 3. It is thus evident that even prolonged treatments at 400°C do not produce a very advanced sintering state.

Owing to the strains introduced by powdering and pressing, electric conductivity is correspond-

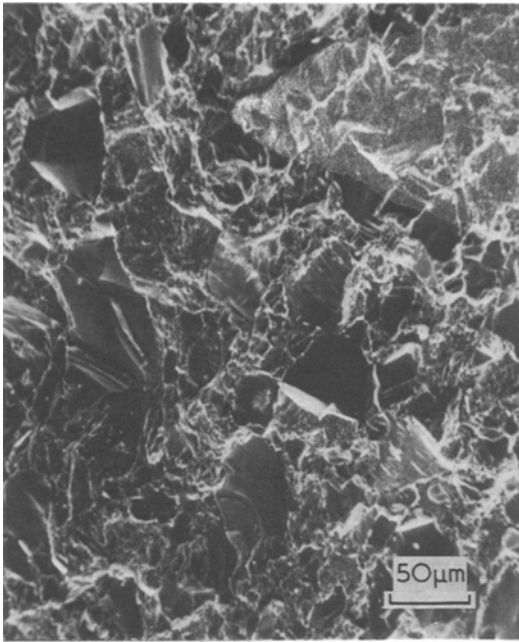


Figure 1 PbTe doped with 0.055 mol% Ag_2Te after powdering and pressing $\times 300$. Typical view of the fragment distribution.

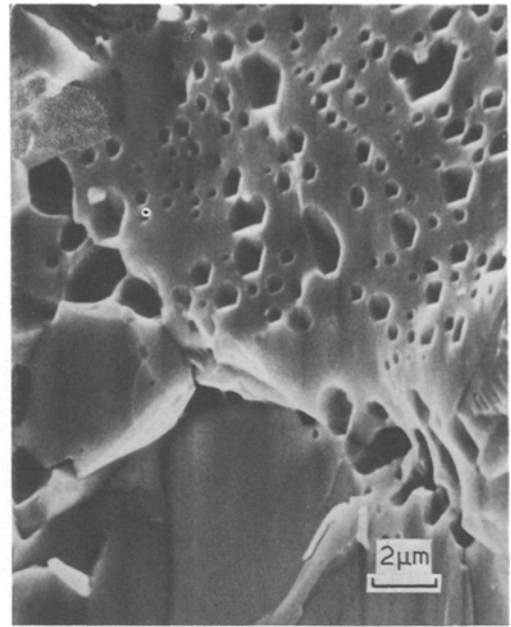


Figure 3 PbTe doped with 0.05 mol% PbBr_2 after 310 h sintering; $f_v = 0.10$, $\times 5000$.

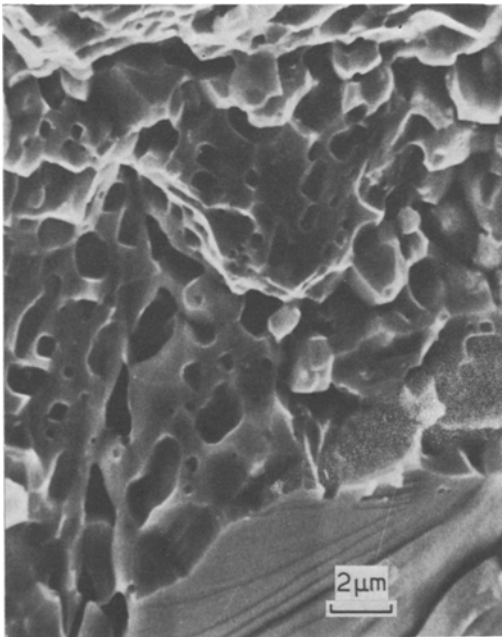


Figure 2 Stoichiometric PbTe, after 310 h sintering; $f_v = 0.15$, $\times 5000$.

ingly very low (see below); however, a definite increase in conductivity can be seen after 300 h annealing.

3.2. Hall effect measurements

3.2.1. Stoichiometric PbTe and Ag_2Te -doped PbTe

Fig. 4a shows a comparison between the $R_H = R_H(T)$ values at $77\text{ K} \leq T \leq 300\text{ K}$ of stoichiometric PbTe and Ag_2Te -doped PbTe samples (curves 1, 2 and 3 respectively), which were later powderd and pressed (curves 1', 2', and 3' respectively). When compared with starting monocrystal variations, it was seen that there was a greater decrease in the p -type carrier concentration in the pressed samples which was calculated using the approximate formula $R_H = 1/pe$. In fact, there was a decrease of $p = 2$ to $6 \times 10^{18}\text{ cm}^{-3}$ (curves 2 and 3) to one order of magnitude lower (curves 2' and 3'). Even NMR measurements indicated [4] that p -type PbTe with a $4 \times 10^{18}\text{ cm}^{-3}$ concentration showed a reduction in the number of carriers and even the disappearance of free carriers after powdering.

We have also seen that some stoichiometric PbTe samples, after being powderd and pressed, showed a reversal in the carrier sign up to an electron concentration of $n = 10^{18}\text{ cm}^{-3}$ (cf. curves 1 and 1').

It is known that PbTe may be either p - or n -type according to the Pb/Te stoichiometric ratio (an excess of Pb relative to the stoichiometric com-

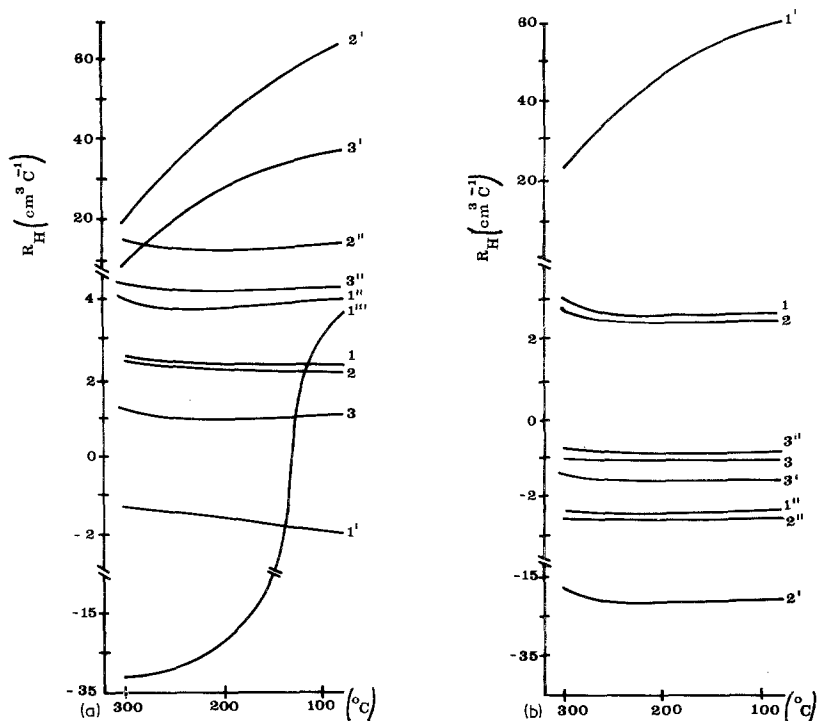


Figure 4 Hall constant versus temperature. (a) 1, stoichiometric PbTe; 2, as above; 3, 0.022 mol% Ag_2Te -doped PbTe; N' , $2'$ and $3'$ correspond to 1, 2 and 3, respectively, after powdering and pressing; $1'''$ corresponds to $1'$ after 50 h annealing; $1''$, $2''$ and $3''$ correspond to $1'$, $2'$ and $3'$ after 310 h annealing. (b) 1 and 2, air-quenched PbTe doped with 0.05 mol% PbBr_2 ; 3, PbTe doped with 0.05 mol% PbBr_2 kept for 1 h at 800°C ; $1'$, $2'$ and $3'$ corresponds to 1, 2 and 3, respectively, after powdering and pressing; $1''$, $2''$ and $3''$ correspond to $1'$, $2'$ and $3'$, respectively, after 310 h annealing. After annealing all samples are water-quenched.

position makes the material *n*-type [5]. Since a compositional variation (loss of Pb) or contamination (the oxygen from the atmosphere is a *p*-type dopant [6]) is not possible during a powdering process performed at room temperature, two alternative hypotheses can be made: (a) the decrease in the hole concentration might be due to the separation of and the formation of a less electrically active tellurium form during the powdering process, or (b) as suggested in [4] the strains caused by the sintering process may introduce donor levels in the gap. In order to verify which of these two hypotheses are more probable, we have periodically examined the *n*-type samples which had been submitted to annealing in a neutral atmosphere. After about 50 h annealing the Hall constant reverses its sign with temperature variation; the sample which was *p*-type at a low temperature became *n*-type at a higher temperature (curve $1'''$). Therefore, it cannot be stated that powdered PbTe acquired *n*-type conductivity because of the partial precipitation of Te in an electrically inactive form. The re-

dissolution of these precipitates by annealing would have shown, contrary to what was in fact seen, the existence of acceptor levels at the higher temperatures, while an *n*-type conductivity would have still existed at lower temperatures.

3.2.2. PbBr_2 -doped PbTe

The transport properties of PbBr_2 -doped PbTe vary considerably according to the thermal treatment applied during solidification. Curves 1 and 2 of Fig. 4b show the behaviour of $R_H = R_H(T)$ in PbBr_2 -doped PbTe polycrystals while curves $1'$ and $2'$ show the powdered and pressed ones.

The polycrystalline ingots were obtained by melting the components which were then submitted to air quenching after a few hours. The polycrystal gives evidence of *p*-type carriers with a concentration of about 10^{18} cm^{-3} . Even the literature [7] has reported that for the PbBr_2 dopant the *p* to *n* variation is obtained only when an excess of Pb was added. It must be added, however, that the cooling process was not controlled [7]. On

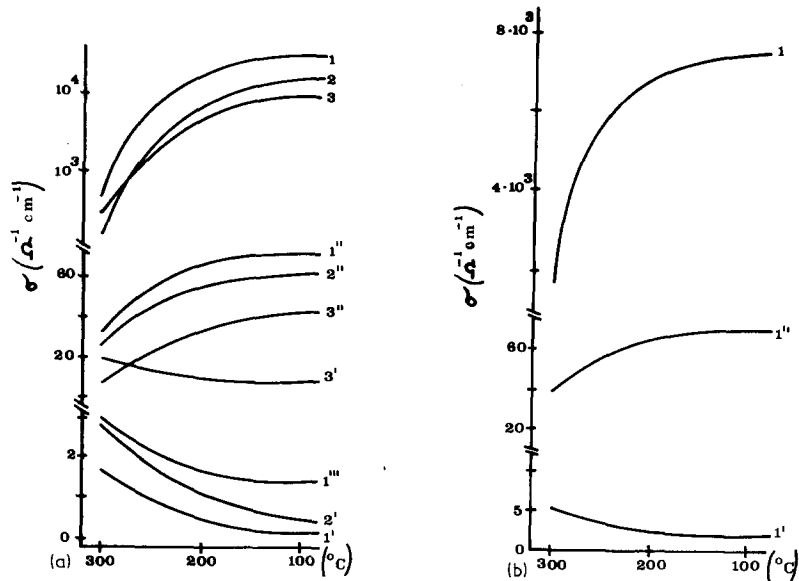


Figure 5 Electrical conductivity versus temperature. (a) 1, PbTe monocrytals; 2, PbTe monocrytals; 3, PbTe monocrytals doped with 0.022 mol% Ag_2Te ; 1', 2' and 3' refer to 1, 2, and 3 respectively, after powdering and pressing; 1'', 2'' and 3'' refer to 1', 2' and 3', respectively, after 310 h annealing. (b) 1, PbTe polycrystal (*n*-type) doped with 0.05 mol% PbBr_2 ; 1' corresponds to 1 after powdering pressing; 1'' corresponds to 1' after 310 h annealing.

the other hand, a hole concentration of about 10^{18}cm^{-3} is typical of the first-to-freeze undoped PbTe once the solidification from the stoichiometric melt, using Bridgman or Czochralski methods, has taken place. This behaviour can be explained by the fact that PbTe has an invariant melting point in the tellurium-rich regions of the phase diagram [8]. Therefore, the solid, which solidifies first, has a composition which corresponds very closely to that of the invariant melting point, i.e. it is rich in tellurium. The doping substance may separate during uncontrolled cooling with the formation of minority phases rich in electrically less-active lead. If this is true, their dissolution in the matrix of the polycrystal should result in an increase in hole concentration. In fact a polycrystal kept for about 300 h at 400°C showed an *n*-type carrier concentration (curve 3).

The same polycrystal which when freshly sintered has $p = 10^{18} \text{cm}^{-3}$ (curves 1 and 2) showed, after powdering and pressing, a decrease in the hole concentration (curve 1') and in some samples even *n*-type carrier concentration (curve 2'). This behaviour is similar to that of the samples seen in the previous sections.

If, after components are melted, the temperature is lowered slowly or maintained at 800°C for a few hours [1–3] the polycrystal ingots were *n*-type (curve 3). The electron concentration

increases with annealing time at 800°C . Upon comparison these *n*-type polycrystals, when powdered and pressed, showed fluctuations in the *n*-type carrier concentration from 10^{18} to 10^{19}cm^{-3} ; it is possible, however, that these fluctuations may have already been present in the starting ingot. Therefore until we are sure of having completely microhomogeneous samples, these fluctuations cannot be attributed to powdering.

3.3. Electrical conductivity

Along with the classical process of scattering due to phonon–phonon, phonon–electron, and point defect interactions, it seems that sintering introduces an additional scattering mechanism [2, 9, 10].

It has not been firmly established whether the enhanced preferential phonon scattering in the sintered structure is due to size or another type of effect or to a combination of effects. The fact is that all the samples examined showed a considerable increase in resistivity after being powdered and pressed (see Fig. 5a and b). These values can be used to calculate Hall mobility $\mu = R_{\text{H}}\sigma$, versus temperature, thus it then becomes apparent that the characteristic behaviour of PbTe monocrytals and polycrytals expressed by the formula $\mu = \mu_0 T^{-n}$ with *n* variable at about 2 to 3 [11] does

not occur. Mobility values for the pressed samples were very low: usually $\mu < 100 \text{ cm}^2 \text{ V}^{-1} \text{ sec}^{-1}$ at room temperature.

3.4. Effect of annealing

After about 300 h annealing at 400°C , the sintering process was still not in an advanced state. However, transport property variations were seen. Figs. 4 and 5 show the $R_H(T)$ and $\sigma(T)$ values, respectively, in powdered, pressed and sintered samples after about 300 h annealing. As seen, stoichiometric and Ag_2Te -doped samples tend to eliminate the donor levels introduced during powdering (the hole concentration increases; curves 1", 2", 3" in Fig. 4a. We have not yet seen what are the long-term values which the properties of Ag_2Te -doped lead telluride acquire.

After 300 h annealing, all the PbTe samples doped with PbBr_2 were n -type (curves 1", 2", and 3" in Fig. 4b) no matter what starting polycrystal was used. For higher annealing times the electron concentration increased until it reached about 10^{19} cm^{-3} after 1000 to 1500 h. Analogous to what has already been noted for the corresponding polycrystals (Section 3.2) this behaviour was due to the segregated dopant settling in an electrically active position (i.e. solubility). At the same time electrical conductivity tended to improve in all the samples, although the values were very different from those found in the starting materials (see Figs 4 and 5a).

It is probable that the conductivity increase depends upon an improved though incomplete sintering state. The conductivity differences found between different samples might also be attributed to different sintering states. Since the final sintering state was not reached, as confirmed by the presence of intergranular channels and open porosity, conductivity was still low. The large number of both open and closed porosities, the great reticular deformation present in the grains, the tension at the grain boundaries among which numerous channels are still present, formed a highly irregular system, in which there was a considerable density of vacancies and dislocation; all this is presumably responsible for the low conductivity found in these materials and thus primarily for the instability of their thermoelectrical properties.

In order to further verify the effect of the dopant on conductivity and on sintering speed, powders of previously sieved and homogenized

samples will be prepared, so that particle and monocrystal fragment size will be uniform and evenly distributed.

4. Conclusions

It has been noted that the PbTe transport properties submitted to sintering, in which no partial constituent evaporation exists, can be considerably different from those of the starting material. The following points were noted:

(1) for p -type stoichiometric or Ag_2Te -doped materials the powdering operation appears to introduce donor levels in the gap. Some p -type polycrystalline samples show the cross-over of carrier sign when powdered and pressed;

(2) PbBr_2 -doped sintered polycrystal showed an n -carrier concentration which was dependent on the degree of dopant solubility in the matrix; a non-controlled cooling of the melt favoured the segregation of the dopant until it had no effect on the transport property. Therefore, the pressed material may have an n -type conductivity when an n -type starting material was used or when polycrystals of an inferior quality with a strongly segregated dopant were used. In this latter case the n carriers were not supplied by the dopant, but were a function of the concentration of donor levels which are caused by powdering;

(3) annealing tends (a) to eliminate donor levels in p -type sintered materials, (b) to increase the electron concentration in sintered polycrystal materials with PbBr_2 -type donors, and (c) to improve electrical conductivity in all those materials which have a low conductivity when powdered and pressed. However, a 400°C sintering temperature, chosen so as to avoid an evaporation process which might have varied the chemical composition of the matrix, was not high enough to complete the sintering process. A more thorough investigation of the relationship between sintering parameters, sintering stage and electrical conductivity is under way in order to pin-point the best thermal treatments necessary to obtain a well sintered material with optimal and stable thermoelectrical and conductivity properties.

References

1. R. W. FRITTS, in "Thermoelectric Materials and Devices", edited by I. B. Cadoff and E. Miller (Reinhold, New York, 1960) p. 143.
2. S. R. GUPTA and H. SINGH, *Phys. Stat. Sol. (a)* 8 (1971) 267.
3. V. FANO, G. MIGNONI and R. PERGOLARI, *Mater.*

- Chem.* **4** (1979) 507.
4. C. R. HEWES, M. S. ADLER and S. D. SENTURIA, *J. Appl. Phys.* **44** (1973) 1327.
 5. R. F. BREBRICK and R. S. ALLGAIER, *J. Chem. Phys.* **32** (1960) 1826.
 6. W. D. LAWSON, *J. Appl. Phys.* **23** (1952) 495.
 7. T. L. KOVAL'CHIK and I. P. MASLAKOVETS, *Sov. Phys. Tech. Phys.* **1** (1957) 2337.
 8. M. P. GOMEZ, D. A. STEVENSON and R. A. HUGGINS, *J. Phys. Chem. Solids* **32** (1971) 335.
 9. J. E. PARROTT, *J. Phys. C. Solid Stat. Phys.* **2** (1969) 147.
 10. H. J. GOLDSMID and A. W. PENN, *Phys. Letters* **27A** (1968) 523.
 11. YU. I. RAVICH, B. A. EFIMOVA and I. A. SMIROV, in "Semiconducting Lead Chalcogenides", edited by L. S. Still'bans (Plenum Press, New York, 1970) p. 91.

Received 12 July and accepted 3 October 1979.