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The sintering of lead telluride

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Scanning electron micrographs, carrier concentration and mobility measurements of sintered doped and undoped PbTe powder compacts are presented as the basis for a qualitative description of the origin of the electrical property change which takes place in powder technique fabrication. A tentative explanation of the changes in the electrical and analogously in thermoelectrical properties, has been given as being due to an increase of the dislocation density when crushing and pressing take place. These dislocations produce a large concentration of electrically different active point defects when they intersect. An additional n-type carrier increase, during firing, confirms this hypothesis.

1. Introduction

To date the main differences between monocrystals and sintered PbTe thermoelectric materials, from both the commercial and efficient point of view, has still not been established. In part this is due to the fact that the obtaining of well sintered lead telluride for practical purposes is still an open question. In fact, many sintering parameters, which have still not been analysed can significantly affect the basic properties of these materials. It has been shown [1] that no sintering can be carried out when temperatures, low enough to eliminate the evaporation of constituents, are used. In this work we analyse those pressed undoped and NaTe doped p-type lead telluride samples, submitted to the sintering process at higher temperatures (650 to 750° C), which are the most suitable for sintering. These temperatures have been chosen for two reasons: (1) 750° C is high enough to induce a satisfactory sintering process; (2) 650° C is low enough so that the electrical property change, associated with the structural variation, can be seen in detail. In this way, some information about the origin of the defects which mainly affect the sintered material properties can be obtained.

2. Experimental techniques

2.1. Materials

Undoped and NaTe doped PbTe single crystals were used as starting materials. The doped monocrystals were grown from a PbTe + 0.5 mol % NaTe melt composition. All monocrystals were synthesized by the Bridgam technique using a 1.8 cm h^{-1} growth velocity. The first to freeze solids were crushed in an agate mortar. For preparation of pressed samples, powders were sieved to obtain 25 to 30 μm grain sizes. The powders were pressed at 200 kg cm^{-2}.

2.2. Thermal treatments

Two sets of samples submitted to the sintering process at 650 and 750° C, respectively, were examined. The thermal treatment was carried out in quartz tubes in a non-oxidizing atmosphere (hydrogen or argon). The maximum sintering time was about 92 h.

2.3. SEM analysis and electrical measurements

Freshly fractured surfaces of both as-pressed and thermal treated specimens were examined by scanning electron microscopy (SEM). Statistical

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measurements of some parameters on micrographs were carried out by using optical stereology methods [2]. These parameters are: f_v = the volumetric fraction of the voids, and $\bar{d}$ = the average dimension of the monocrystalline fragments and/or grains. The Hall effect and the electrical conductivity are measured by the techniques described by Fano [3].

3. Results and discussion

3.1. As-pressed materials

Under SEM examination, the as-pressed specimens appear to be starting single crystal fragments, which are of the selected dimensions (25 to 30 μm). It is difficult to calculate the void fraction among these fragments because very small fragments are formed by the sharp corners of the starting fragments when powders are pressed. There are no significant differences between the doped and the stoichiometric PbTe pressed materials.

3.2. 650° C thermal treatment

3.2.1. Influence of sintering time

After 5 h treatment all undoped samples showed significant changes but the structure was still very disordered. Strong grain distortions with very widespread porosity, which was canalized and interconnected, existed. Many cavities were also present inside the fragments. In shape, these cavities ranged from circular to square sections, according to the cubic PbTe crystalline structure. The grain size was not uniform, however, the corners were rounded, often having an egg-like shape, typical of the first stages of the sintering process (Fig. 1). When the treatment time was increased up to 40 h, the f_v behaviour was erratic: the f_v values were very scattered even if they tended to decrease (Fig. 2). Probably these anomalies are due to the competition among the smallest fragments during the densification process. The larger fragments do not take part in this. After 40 h, the decrease in f_v was significant. On the other hand, after the early growth stages had terminated, the grain sizes reached a value of about 40 μm; further growth seemed to be inhibited. After 90 h, the grains assumed an almost polygonal shape with sharp corners, many pores disappearing within the grains because they probably migrated towards the edge. In other words, many structural stresses appeared to relax, but the solid had still not attained those characteristics which make for well sintered materials (Fig. 3a).

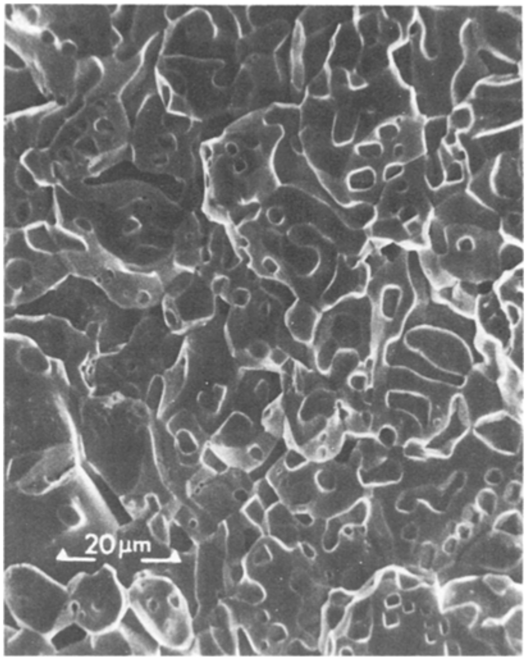

Figure 1 PbTe after 5 h annealing at 650° C.

3.2.2. The influence of the dopant

The dopant seemed to favour the thermal densification process. The following characteristics could be ascribed to the dopant: the porosity was always lower than that of the stoichiometric composition samples. The f_v decrease, as a function of the treatment time increase, was sharper and more regular. For longer treatments the porosity inside the crystals decreased shifting towards the grain boundaries. The crystals had a more uniform shape. In both compositions, the crystal dimensions were the same. Therefore, it stands to reason that the most compact sample would be the doped one which had been submitted to the sintering for the longest length of time. However, the structure integrity was compromised by extensive cracks (Fig. 3b) which separated good compact regions. One can suppose that the improvement of the sintering in these regions is due to the increase of the surface energy. If this is true, an increase of dopant concentration is expected to appear on the grain surface. Assuming that no different trends exist between the molten and solid state, we measured the sodium concentration on the surface and within the bulk of molten NaTe doped

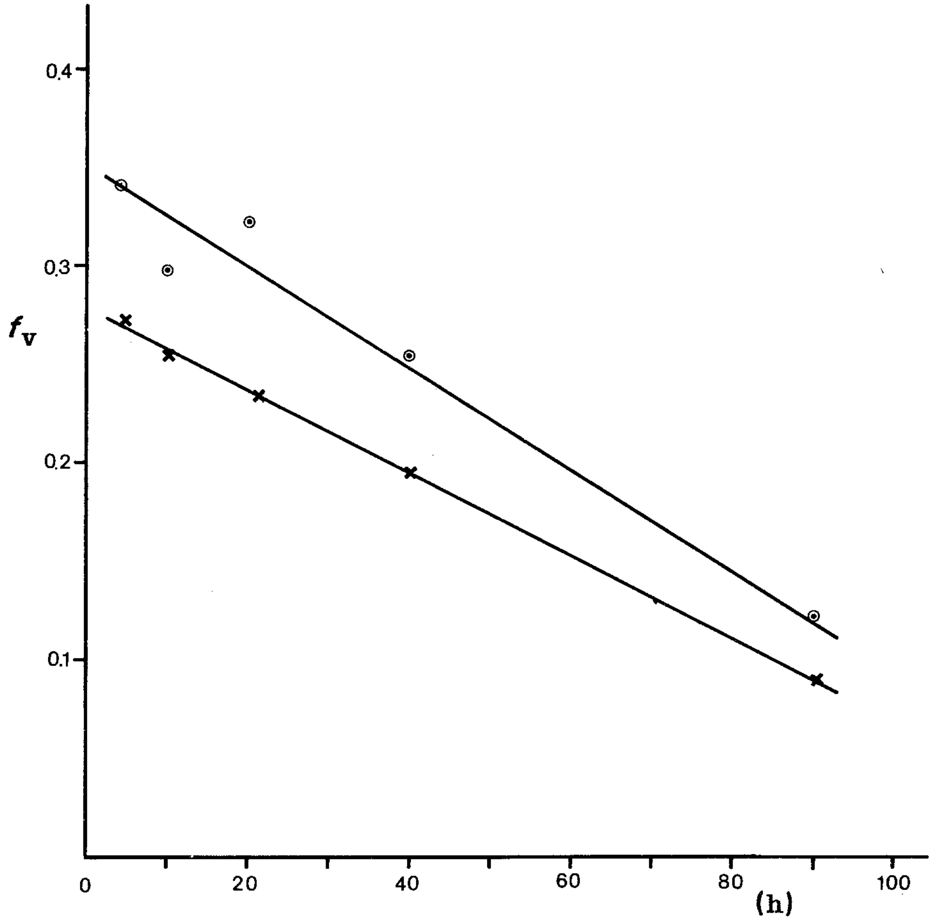

Figure 2 f_v as a function of annealing time. ⊙, Undoped PbTe. ×, Na-doped PbTe. The temperature is 650° C.

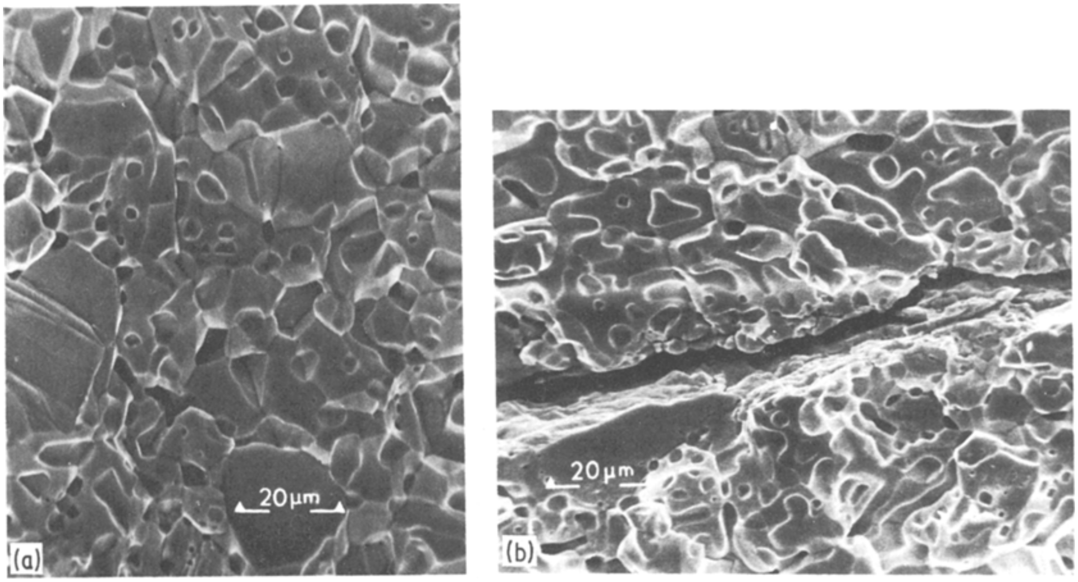

Figure 3 Annealing after 92 h at 650° C. (a) Undoped PbTe. (b) Extensive cracks in Na-doped PbTe.

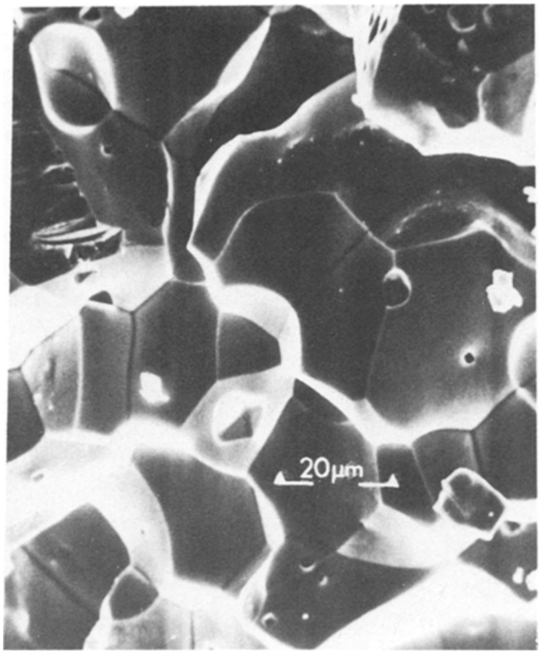

Figure 4 PbTe after 90 h annealing at 750° C.

specimens by absorption flame spectroscopy. The surface samples were obtained by scraping the water quenched doped molten materials. The sodium surface concentration was always greater than the bulk concentration. This fact lends support to the above mentioned hypothesis that the dopant increases the sintering process by lowering the surface energy. The stresses associated with this sintering seem to produce extensive cracks. Thus, the mechanical properties of doped sintered materials are poorer than those of the stoichiometric samples.

3.3. 750° C thermal treatment

3.3.1. Influence of the annealing time

The samples annealed at 750° C for different lengths of time (27, 45 and 90 h) did not show significant structural variations. Clearly most of the evolutionary processes occurred within the early stages of annealing. Generally the samples had a satisfactory densification and showed polygonal and well packaged crystals. The volumetric fraction of the voids was about 5 to 7%. This fraction could be ascribed mainly to the intergranular interstices, which were not numerous, but were sometimes large. However, the prolonged thermal treatment at 750° C was not superfluous since after 92 h there was a decrease of the pores inside the grains. Furthermore, the grains had larger sizes and more often manifested transgranular fractures (Fig. 4).

3.3.2. The influence of the dopant

The dopant effect was similar to that observed in the samples treated at 650° C, i.e. the dopant exerted an ordered influence on the microstructure. In fact, the microstructure of the doped materials was more uniform, but the macrostructure still showed some cracks, which affected the mechanical properties to a lesser extent. The f_v values of the doped and undoped samples were about equal, but those of the stoichiometric sample were more scattered; in both cases, no correlation between f_v and treatment time could be made.

3.4. Electrical measurements

A wide range of electrical behaviour can be imposed upon PbTe and this depends upon the mechanical and thermal history, which introduces and/or removes some defects. The influence of point or line defects are widely reported in the literature [4].

Now we will trace the electrical behaviour trend of PbTe throughout its thermal history, during which large line and point defect contributions are supposedly introduced by powdering. For simplicity, we will first analyse the undoped materials. After powdering there was a decrease in both the mobility, i.e. σ conductivity ($\mu = R_H\sigma$) and p-type carrier concentration (in some cases there was a reversal of the sign) (see Table III). These facts suggested that the primary cause which affected the transport properties was the large concentration of line

TABLE I Summary of the results of the SEM examination of the samples submitted to annealing at 650° C

Materials	Annealing time (h)	f_v	$\bar{d}$ (μm)
Stoichiometric PbTe	5	0.33	20
	10	0.29	28
	21	0.31	30–40
	40	0.25	30–40
	92	0.12	30–40
Na-doped PbTe	5	0.27	28
	10	0.25	39
	21	0.23	40–50
	40	0.19	40–50
	92	0.091	40–50

TABLE II Summary of the results of the SEM examination of the samples submitted to annealing at 750° C

Materials	Annealing time (h)	f_v	$\bar{d}$ (μm)
Stoichiometric PbTe	27	0.068	50
	45	0.10	50
	90	0.042	50–70
Na-doped PbTe	27	0.064	50
	45	0.056	50–60
	90	0.059	50–70

defects, such as dislocations introduced during the powdering. We shall now examine this assumption by considering the following points.

(a) A significant dislocation-induced resistance caused by the distorted potential connected with edge dislocations is to be expected when the dislocation density is sufficiently high.

(b) The decrease of the p-type carrier concentration indicates that the electron density is increased instead of the hole concentration being decreased. In fact, some additional information can be obtained from the mobility behaviour as a function of temperature $\mu \simeq T^{-\alpha}$, when α is roughly equal to 2.5 for undoped materials and decreases as the dopant concentration increases [4]; this behaviour depends upon the scattering mechanisms within the 80 to 300° C temperature range. In the case of the compacted samples the general shape of these curves is reminiscent of that obtained from samples which were known to be highly compensated. In fact it was found that $\alpha \simeq 1$. This lends considerable support to the hypothesis that an end result of the powdering is the introduction of a large concentration of point defects, such as vacancies and/or interstitials.

(c) Point defects (vacancies and interstitial atoms) arise from the jogs formed by the intersection of dislocations. These point defects affect the electrical properties in different ways: ionization state one or two is ascribed to a donor (tellurium vacancy) or to an acceptor (lead vacancy) while it has been demonstrated theoretically [5, 6] and experimentally [7] that interstitial lead should be a doubly ionized donor and interstitial tellurium should be neutral or a weak donor. If this is true, the n-type carrier concentration increase is to be expected when the PbTe is powdered and pressed. In addition to this, a trail of either vacancies or interstitial atoms, depending on the dislocation sign and the direction in which the dislocations are moving, will be left behind by the thermally activated movement of the jogs. Thus, during annealing the probability of a further n-type carrier increase is very high, and this, in fact, is what actually occurs: starting materials with $p \simeq 5 \times 10^{18}\,\mathrm{cm}^{-3}$ carrier concentration show a decrease of their p-type carrier concentration or a sign crossover (n-type at low temperatures) or an n-type electrical conductivity. The maximum n-type carrier concentration was found to be 10^{20} to $10^{21}\,\mathrm{cm}^{-3}$ (4 samples out of 50). Thus, this n-type carrier generation mechanism can signficantly affect the thermoelectrical properties. The data obtained from the doped materials which are $p = 6\text{–}8 \times 10^{19}\,\mathrm{cm}^{-3}$ before powdering, are in agreement with this behaviour. We observed a reversal of the carrier sign in the 80 to 300° C temperature range in only a few samples (3 out of 50, the same percentage as those undoped powdered materials which reach or exceed $n \simeq 10^{20}\,\mathrm{cm}^{-3}$ during annealing).

(d) After the increase of the mobility due to the electrical conductivity increase during the initial annealing hours, no useful improvement occurred; the mobility oscillated, there were no differences in the behaviour between the two sets (650 and 750° C thermal treatment). Thus it seems that a further improvement of the electrical properties was not dependent upon the interaction between the grains or upon the observed recrystallization. Thus the improvement of the electrical properties is connected with the diffusion out of both the dislocation type line defects and the associated point defects.

4. Conclusions

(a) It has been found that 750° C is suitable for inducing a satisfactory sintering process. This temperature can actually be used during sintering because the constituent evaporation during the process (< 30 h) is negligible. Thus, no significant compositional variation occurs when a bulk of material, commonly used in thermoelectric energy conversion experiments, is involved.

(b) By comparing the undoped and the doped materials it is seen that the poor mechanical properties of the latter seem to be caused by the dopant, which exerts an ordered influence on the microstructure, but also induces extensive cracks.

TABLE III Summary of the mobility and carrier concentration values at RT. There are 100 starting samples (50 undoped samples, 50 doped samples), 25 samples of the same composition for each temperature

Starting materials	Annealing temperature (°C)	Annealing time (h)					
		0		5		90	
		μ	p, n	μ	p, n	μ	p, n
PbTe:							
$p = 2$–$6 \times 10^{18}\,\mathrm{cm}^{-3}$	650	0.1–90	$p \leqslant 4 \times 10^{17}$	30–200	$p \leqslant 10^{17}$ $n \leqslant 10^{17}$	43–210	$p \leqslant 8 \times 10^{16}$ $n^* < 10^{21}$
$\mu = 680$–$1200\,\mathrm{cm}^2\,\mathrm{V}^{-1}\,\mathrm{sec}^{-1}$	750	0.1–90	$p \leqslant 4 \times 10^{17}$	27–190	$p \leqslant 10^{17}$ $n \leqslant 10^{18}$	25–215	$p = 7 \times 10^{16}$ $n^* < 10^{21}$
Na-doped PbTe:							
$p = 6$–$8 \times 10^{19}\,\mathrm{cm}^{-3}$	650	0.5–85	$p = 5$–8×10^{19}	25–160	$p = 6$–9×10^{19}	35–178	$p = 5$–9×10^{19} $n^* < 10^{21}$
$\mu = 200$–$420\,\mathrm{cm}^2\,\mathrm{V}^{-1}\,\mathrm{cm}^{-1}$	750	0.5–85	$p = 5$–8×10^{19}	22–180	$p = 7$–8×10^{19}	38–192	$p = 5$–9×10^{19} $n^* < 10^{21}$

*See text.

(c) In all instances the electrical properties of the best sintered materials are significantly poorer than those of the starting monocrystals. The generation of line type defects such as dislocations during powdering seems to be the origin of this. Recently some attempts have been made to demonstrate that the efficiency of the thermoelectric materials can be increased by using fine grained materials [8, 9]. In this case the phonon thermal conductivity (K) is reduced, since the reduced grain sizes ensure the scattering of the long wavelength phonons. Consequently, the figure of merit $Z = \alpha^2\sigma/k$ (where α is a Seebeck coefficient) increases. Although this approach can be profitable, there are other properties that need to be considered for the PbTe based materials. In fact, some manufacturing methods, such as powdering, produce a wide variation of properties in terms of carrier concentration and mobility change induced by the above mentioned line defects. The improvement of the sintered material properties seems to be related to the decrease of these defect concentrations.

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