

Mechanical properties of PbTe-based thermoelectric semiconductors

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This paper is concerned with the mechanical properties of PbTe and $\text{Pb}_{1-x}\text{Sn}_x\text{Te}$ compounds and their correlation with the respective charge carrier concentrations. Single-crystals and samples prepared by powder metallurgy display similar general trends. It was found that although there is a similar electronic behavior (constant scattering factor of -0.5) for the various compositions examined, the mechanical properties of the compounds are completely different.

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PbTe-based compounds are well-known n-type and p-type compounds for thermoelectric applications in the 50–600 °C temperature range. The thermoelectric properties of these compounds are highly dependent on the carrier concentration, the temperature and the preparation technique. Compounds solidified from a stoichiometric melt exhibit a carrier concentration of the order of 10^{17} – 10^{18} cm^{-3} at room temperature [1]. The carrier concentration can be changed by thermal annealing in a Pb-rich (for n-type conductivity) or a Te-rich (for p-type conductivity) atmosphere. When samples with carrier concentrations higher than 10^{18} cm^{-3} are required, e.g. for thermoelectric energy conversion applications, doping elements are added. PbI_2 is the most frequent donor in PbTe, while Na is the most frequent acceptor. It is noteworthy that at different temperatures, different carrier concentrations yield maximal thermoelectric efficiency values. Therefore, it is obvious that for operation at different temperatures, thermoelectric materials with different carrier concentrations are needed.

Mechanical properties are also important in determining the performance of the thermoelectric materials since the latter are subject in the course of their operation to various mechanical and thermal stresses.

In single-crystal (SC) PbTe compounds [2,3], the microhardness is relatively constant and equal to

~30 HV for the various carrier concentrations examined. In heavily doped p-type PbTe with a hole concentration higher than 10^{19} cm^{-3} , however, a sharp increase in microhardness takes place.

It has been established previously [4] that n-type PbTe exhibits good stability, reasonably good mechanical properties and can be joined to metallic shoes with stable bonds, in contrast to p-type PbTe. The latter becomes unstable at high temperatures, is very susceptible to poisoning during processing and operation, has poor mechanical properties and is difficult to bond. p-Type $\text{Pb}_{1-x}\text{Sn}_x\text{Te}$ alloys with x values in the range of 0.1–0.5 [5] have been suggested as appropriate substitutes for Na-doped PbTe. These pseudo-binary compounds have hole concentrations of about 10^{20} cm^{-3} . Cui et al. [6] have recently reported that powder metallurgy (PM)-based $\text{Pb}_{1-x}\text{Sn}_x\text{Te}$ alloys display high microhardness values (95 HV), higher than those reported for SC heavily Na-doped PbTe (60 HV) [2,4]. These high microhardness values were reported, however, for non-perfect materials with relatively low-density ($\leq 93\%$ of theoretical) and containing dispersed micro-oxides in the matrix.

PM-based PbTe compounds are frequently used in practical applications. In such materials, however, the mechanical properties, to the best of our knowledge, have not been reported. Data are available only for SC PbTe and PM-prepared $\text{Pb}_{1-x}\text{Sn}_x\text{Te}$.

In the present work, the mechanical properties of both n- and p-type PbTe compounds, prepared by PM

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and SC growth, were examined and compared. In order to evaluate the mechanical properties of p-type $\text{Pb}_{1-x}\text{Sn}_x\text{Te}$ for practical thermoelectric applications as compared to Na-doped PbTe, samples with x values in the range of 0–0.6 were prepared by the PM approach. All samples had nearly full density ($\sim 98\%$ of theoretical) with no second phase precipitates.

- (i) SC PbTe compounds with Te excess or doped with PbI_2 and Na were grown using the Czochralski technique as reported elsewhere [7]. A $\langle 100 \rangle$ oriented seed PbTe crystal was used.
- (ii) PM-prepared PbTe samples with Te excess or doped with In, PbI_2 and Na as well as p-type $\text{Pb}_{1-x}\text{Sn}_x\text{Te}$ alloys were prepared using the same techniques as previously published [5,8]. The density of the specimens was higher than 98% of the theoretical and the average grain size was 25–30 μm .
- (iii) The electronic transport properties of the samples were obtained as follows: the measurements of the Seebeck coefficient and the electrical resistivity were carried out in a furnace under an argon atmosphere. The Hall effect experiments were performed in an electromagnet of 1 T, under a vacuum of 10^{-5} Torr, for determination of the free carrier concentration.
- (iv) Microhardness was measured by Vickers indenters using a Buehler microhardness standard machine. Indenting loads were calibrated at the range of 1–300 gF and fixed to 10 gF for single-crystals and 50 gF for sintered samples. All results were obtained at room temperature. The microhardness value was taken as an average of 10 indentations for each sample and the standard deviation was calculated.
- (v) Stress–strain behavior was determined by compression experiments. The samples were tested in a Zwick-1445 machine, at room temperature, at a crosshead speed of 3 mm min^{-1} . All specimens were 6.3 diam $\times$ 5 mm cylinders.
- (vi) Three-point bending tests were performed in the Zwick-1445 machine at room temperature and at

a crosshead speed of 3 mm min^{-1} . The samples were $9 \times 2 \times 1 \text{ mm}$ box shaped. The tests were based on ASTM C1161 standard; however, because of the difficulty in manufacturing standard size samples the reported results are relative and in arbitrary units.

All the measured transport and mechanical properties, namely the carrier concentration (n or p , according to the conduction type), Seebeck coefficient (α), electrical resistivity (ρ), microhardness (HV), maximal compression stress (σ_{uts}), strain at maximal compression stress (ϵ_{uts}) and the bending strength (σ_{B}), are summarized in Table 1.

Stress–strain curves for n- and p-type PbTe PM-prepared samples with different carrier concentrations are presented in Figure 1.

The room temperature Seebeck coefficient values of all of the prepared samples follow the general trend of a single-band model using a scattering parameter r of -0.5 and an effective mass of $0.3 m_0$ (the electronic rest mass), as presented in Figure 1.

The calculated results using a single-band model in Figure 2 are based on the following equations:

$$\alpha = \pm \frac{k}{e} \left[\frac{\left(\frac{5}{2} + r\right) F_{\frac{5}{2}+r}}{\left(\frac{3}{2} + r\right) F_{\frac{3}{2}+r}} - \eta \right] \quad (1)$$

$$n, p = \frac{4}{\sqrt{\pi}} \left(\frac{2\pi \cdot m^* \cdot kT}{h^2} \right)^{3/2} \cdot F_{1/2} \quad (2)$$

where e is the charge on an electron, h is Planck's constant, k is the Boltzmann constant, F_r is the Fermi integral, η is the reduced Fermi potential and m^* is the effective mass.

The agreement between all of the measured Seebeck coefficient values in Figure 2 and the calculated curve indicates that all of the compositions examined give a similar scattering factor of -0.5 . This value indicates scattering of the charge carriers by the thermal vibrations of the lattice (phonons) in an acoustic mode. The same mechanism of carrier scattering at all of the compositions examined suggests similar types of atomic

Table 1. Measured transport and mechanical properties for the PM-prepared and SC samples

Sample	$n/p \text{ (cm}^{-3}\text{)}$	$\alpha \text{ (}\mu\text{V/K)}$	$\rho \text{ (m}\Omega \text{ cm)}$	Hv	$\sigma_{\text{uts}} \text{ (MPa)}$	ϵ_{uts}	$\sigma_{\text{B}} \text{ (AU)}$
PbTe(Te)	$1 \times 10^{17} \text{ (p)}$			30	122	0.14	
$\text{Pb}_{0.9}\text{Sn}_{0.1}\text{Te}$	$5 \times 10^{18} \text{ (p)}$	162	2.87	38	120	0.135	
$\text{Pb}_{0.8}\text{Sn}_{0.2}\text{Te}$	$9 \times 10^{18} \text{ (p)}$	100	1	43			
$\text{Pb}_{0.7}\text{Sn}_{0.3}\text{Te}$	$5 \times 10^{19} \text{ (p)}$	74	0.75	50	118	0.13	
$\text{Pb}_{0.6}\text{Sn}_{0.4}\text{Te}$	$7 \times 10^{19} \text{ (p)}$	50	0.5	48	108	0.123	
$\text{Pb}_{0.5}\text{Sn}_{0.5}\text{Te}$	$1 \times 10^2 \text{ (p)}$	35	0.34	49	80	0.105	
$\text{Pb}_{0.4}\text{Sn}_{0.6}\text{Te}$	$1.2 \times 10^2 \text{ (p)}$	30	0.25	50			
PbTe(Na)	$1 \times 10^2 \text{ (p)}$	49	0.28	71	120	0.06	12
PbTe(In)	$3 \times 10^{18} \text{ (n)}$			36			
	$5 \times 10^{18} \text{ (n)}$			34	130	0.18	28.5
PbTe(PbI ₂)	$6.5 \times 10^{18} \text{ (n)}$	150	0.6	33	150	0.25	32
	$2.2 \times 10^{19} \text{ (n)}$	80	0.3	34			40
	$4.2 \times 10^{19} \text{ (n)}$	65	0.25	32			41
	$6 \times 10^{19} \text{ (n)}$	45	0.19	33			31
PbTe(Na) ^a	$2 \times 10^{20} \text{ (p)}$	40	0.17	87			
PbTe(Te) ^a	$1 \times 10^{17} \text{ (p)}$			29			
PbTe(PbI ₂) ^a	$5 \times 10^{19} \text{ (n)}$	75	0.27	26			

^a S.C grown.

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