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Thermoelectric properties of p-type PbTe-PbSe alloys

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The thermoelectric properties of p-type PbTe-PbSe alloys have been studied as a function of temperature. The high-temperature figures of merit of several alloy compositions have been found to be significantly greater than PbTe. This improvement is related to the ability to achieve higher doping levels in these alloys and, hence, superior electrical properties at elevated temperatures.

It has been shown that the use of dilute alloys [1] of lead and germanium tellurides, which reduce the thermal conductivity without significantly degrading the electrical properties, can result in superior performance thermoelectric materials. This approach led to the development of n-type PbTe-GeTe alloys having figures of merit 35 to 40% greater than PbTe [1]. However, p-type alloys of that system could not be prepared with large enough carrier concentrations for operation at temperatures in excess of 500 K. Therefore, the alloy system PbTe-PbSe was reinvestigated since highly doped p-type alloys can be prepared in this system [2, 3]. As in the case of the PbTe-GeTe system, dilute alloys were investigated.

A series of PbTe-PbSe alloy samples in the range of 0 to 25 mol % PbSe were prepared by the vertical Bridgman technique, containing 0.5 to 1.0 mol % Na as the p-type dopant. The room-temperature properties of these samples are listed in Table I, together with data on p-type PbTe prepared in this laboratory.

TABLE I Composition, dopant concentration and room-temperature electrical properties of p-type PbTe-PbSe alloys

Sample ○	Composition (mol % PbSe)	Dopant (mol %) Na	Electrical resistivity ($10^{-4}\Omega$-cm)	Seebeck coefficient (μV/deg^{-1})
160	5	0.5	4.50	+ 71.0
161	10	0.5	4.70	+ 70.5
163	25	0.5	5.32	+ 57.0
83	5	0.7	4.04	+ 50.0
97	5	0.7	4.35	+ 57.5
149	10	0.7	4.45	+ 57.0
150	15	0.7	4.25	+ 59.5
188	5	1.0	3.58	+ 49.5
189	10	1.0	4.0	+ 47.0
168	0	0.7	3.12	+ 61.5
170	0	1.0	3.22	+ 57.5

Examination of Table I shows that a sample having 5 mol % PbSe and 0.7 mol % Na has a room temperature Seebeck coefficient of 50.0 μV/°C as compared to 61.5 μV/°C for PbTe. The low Seebeck coefficient is indicative of a high carrier concentration and thus, unlike the PbTe-GeTe alloys [1], these alloys are easily doped for high-temperature operation.

The data in Table I reveal several interesting points: (1) the alloys containing PbSe achieve lower Seebeck coefficients than PbTe for the same dopant concentration and (2) the Seebeck coefficient decreases, at a constant dopant level in the melt, as the mole fraction PbSe increases. Both of these observations suggest that the results are due to an increasing Na Solubility and/or a reduction in the hole effective mass as the amount of PbSe is increased. The effect of a decreasing hole effective mass is such that a lower Seebeck coefficient will result for a constant carrier concentration. This possibility is, however, considered to be a minor effect since we are dealing with alloys containing 25 mol %, or less, PbSe.

The figure of merit of a thermoelectric material is defined as

$$Z = Q^2/\rho k$$

where Q is the Seebeck coefficient, ρ is the electrical resistivity, and k is the thermal conductivity. Improvements in the figure of merit can be achieved by either lowering k or increasing the ratio Q^2/ρ. The temperature dependence

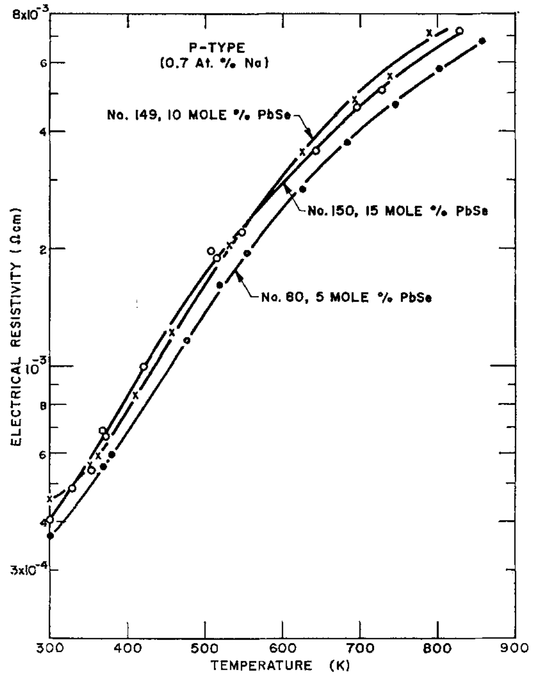

Figure 1 The temperature dependence of electrical resistivity for samples of p-type PbTe-PbSe alloys.

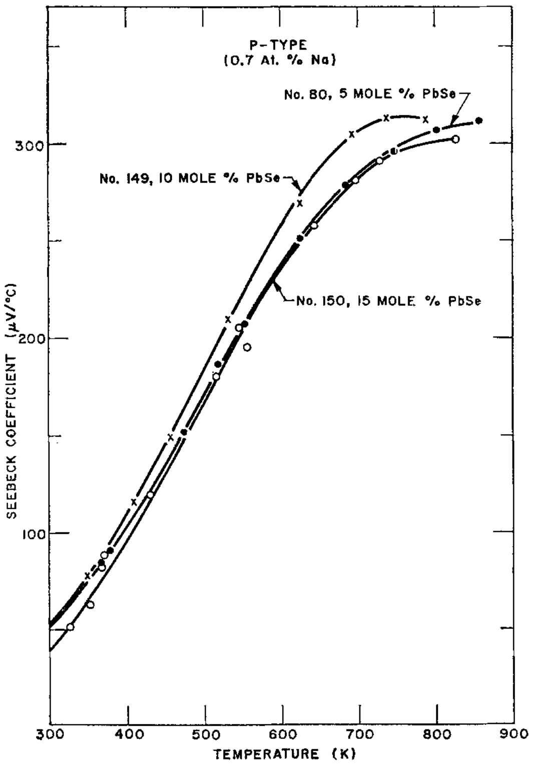

Figure 2 The temperature dependence of Seebeck coefficient for samples of p-type PbTe-PbSe alloys.

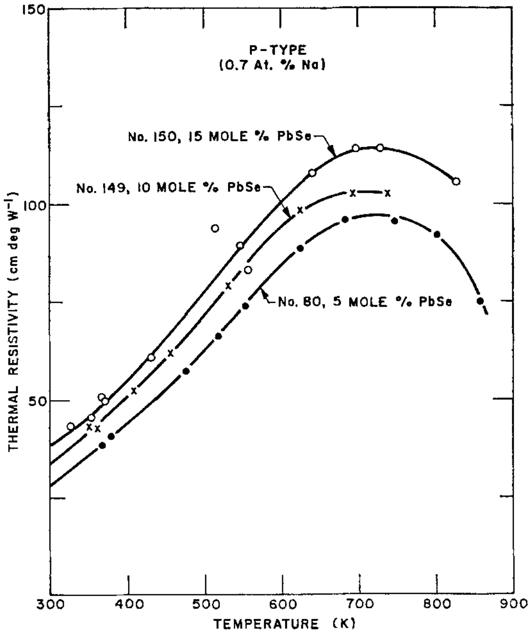

Figure 3 The temperature dependence of thermal resistivity for samples of p-type PbTe-PbSe alloys.

of the thermoelectric parameters for samples containing 0.7 mol % Na were obtained in a diffusivity apparatus described previously [4] and are shown in Figs. 1, 2 and 3. The figure of merit is shown in Fig. 4. The figure of merit peaks at a value of 2.0×10^{-3} deg^{-1}, which is an improvement of approximately 30% over PbTe.

The major contribution to the improvement in figure of merit *is not* the lowering of the thermal conductivity as in the case of the PbTe-GeTe alloys [1]. Rather it results from the ability to achieve higher Q^2/ρ values at elevated temperatures as compared to PbTe. The high-temperature electrical properties, and, therefore, the figure of merit are strongly dependent on the carrier concentration. Increasing the carrier concentration allows the attainment of higher Q^2/ρ values prior to the onset of intrinsic conduction and a corresponding decrease in the figure of merit. This is especially true for the p-type lead salt compounds and their alloys in which the ratio of electron to hole-mobility is greater than one. It is the apparent higher solubility of the p-type dopant in these alloys, therefore, that is responsible for the improvement in the thermoelectric figure of merit. Thus, the high-temperature figure of merit of these

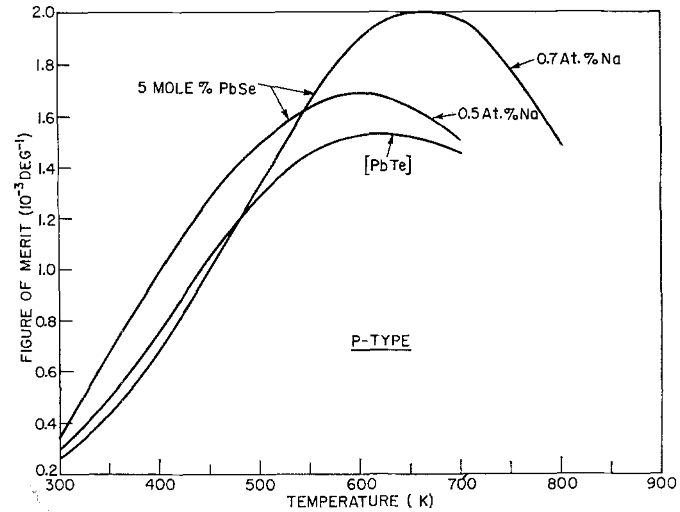

Figure 4 The temperature dependence of figure of merit for samples of p-type PbTe-PbSe alloys. The figure of merit of p-type PbTe is shown for comparison.

alloys is maximum at the highest carrier concentrations.

The electrical resistivity is seen to increase with increasing PbSe content (Table I). This is not unexpected since alloy scattering is known to be operative in this system [2]. The high-temperature figures of merit are nearly identical for alloys containing 5 to 15 mol % PbSe. This results from a counterbalancing of two competitive processes, the decrease in thermal conductivity, and the increase in electrical resistivity. As the mole fraction PbSe increases further, the reduction in thermal conductivity is insufficient to counterbalance the rise in electrical resistivity and the figure of merit decreases. The maximum figure of merit occurs, therefore, for alloys containing 5 to 15 mol % PbSe, doped with at least 0.7 mol % Na.

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