Thermoelectric figure of merit of hetero- and isovalently doped PbSe

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We investigate the thermoelectric power coefficient, electrical conductivity, and thermal conductivity of PbSe doped with chlorine and sodium in the temperature interval 300–950 K. The values of the kinetic coefficients and thermoelectric figure of merit are compared with analogous data for PbTe. An improvement in the thermoelectric parameters of *p*-PbSe is observed at high temperatures after additional isovalent doping by cadmium and manganese impurities. © *1996 American Institute of Physics.* [S1063-7826(96)00812-5]

Thermoelectricity is employed today to solve a fairly broad range of problems. For this reason, in choosing a thermoelectric material we must take into account not only its thermoelectric efficiency but also its cost, range of allowable temperatures, the possibility of donor and acceptor doping, etc. Along with traditional thermoelectric materials, the list of materials that show promise for practical applications has come to include those whose inferior figure of merit is offset by advantages with regard to other parameters. One such material is PbSe, which has the advantage of a melting temperature higher than PbTe. Its thermoelectric figure of merit Z ($Z=S^2\sigma/\varkappa$, where S, σ, and $\varkappa$ are the thermoelectric power coefficient, electrical conductivity, and thermal conductivity, respectively) has not been studied at high temperatures, because the prevailing wisdom is that it must be considerably less than that of PbTe due to its lower mobility and smaller width of the band gap.[1] The question of whether PbSe can be used in thermoelectric generators requires a more careful answer.

In this paper, we report our measurements of the thermoelectric parameters of PbSe in the temperature interval 300–950 K with electrically active impurities of chlorine (n-type) and sodium (p-type). By introducing these dopants we can achieve optimal carrier concentrations and determine maximal values of Z at high temperatures. We compare our experimental results with analogous data for PbTe obtained under the same conditions. We tried additional doping of p-PbSe with the isovalent impurities Mn and Cd as a means of improving its thermoelectric properties. The compositions of the samples we studied are listed in Table I. In Fig. 1 we compare the temperature dependences of the thermoelectric properties of PbSe and PbTe, each with an electron concentration of $\sim 2\times 10^{19}$ cm^{-3} (samples 1 and 3). Curves of the thermoelectric figure of merit Z are plotted in Fig. 2, along with values of Z for yet another pair of samples (2 and 4) with concentrations $\sim 3.5\times 10^{19}$ cm^{-3}. Comparing these curves shows that at moderately high temperatures the difference in thermoelectric figures of merit of the two materials is determined by a competition of two factors: the ratios of the mobilities and thermoconductivities, the first favorable for PbTe, the second for PbSe. The lower mobility in PbSe comes from the contribution to electron scattering from optical phonons, which is larger than in PbTe. The contributions to the mobilities from the interaction of electrons with acoustic phonons are almost the same in the two materials.[2] As T is raised, the optical-phonon contribution to the scattering decreases; hence, the difference in Z for PbSe and PbTe due to this factor becomes smaller. Nevertheless, it remains the decisive factor in making the maximal values of Z higher in PbTe. This is because the compensating factor—the difference in thermal conductivities—disappears much more rapidly with increasing T in PbSe than in PbTe as the optical phonons "switch on" the heat transport, due to the larger value of the mass ratio of the atoms that make up the PbSe lattice.[3]

At high temperatures $T > 800$ K the combination of parameters that determines Z begins to favor PbSe. A comparison of high-temperature data on S and $\varkappa$ for our PbSe and PbTe samples with the same electron concentration (1 and 3 in Fig. 1) shows clearly that, contrary to the expectations mentioned above, the temperature at which the influence of minority current carriers becomes significant is 50–100 °C higher in PbSe than in PbTe, so that Z falls off more smoothly at high temperatures. The difference in values of the maximum Z also gradually decreases, because optimal electron concentrations become higher. Since, as shown in Ref. 2, higher concentrations of current carriers, like the raised temperatures, decrease optical-phonon scattering, the difference in maximum Z decreases as well.

TABLE I.

Sample	Host	Content of isovalent impurities	Concentration of electrically active impurities
1	PbSe	–	0.11 at. % Cl
2	PbSe	–	0.20 at. % Cl
3	PbTe	–	0.135 at. % I
4	PbTe	–	0.24 at. % I
5	PbTe	–	1.75 at. % Na
6	PbSe	–	0.5 at. % Na
7	PbSe	–	1.25 at. % Na
8	PbSe	3 at. % Cd	1.25 at. % Na
9	PbSe	1 at. % Mn	2.0 at. % Na
10	PbSe	5 at. % Cd	2.0 at. % Na

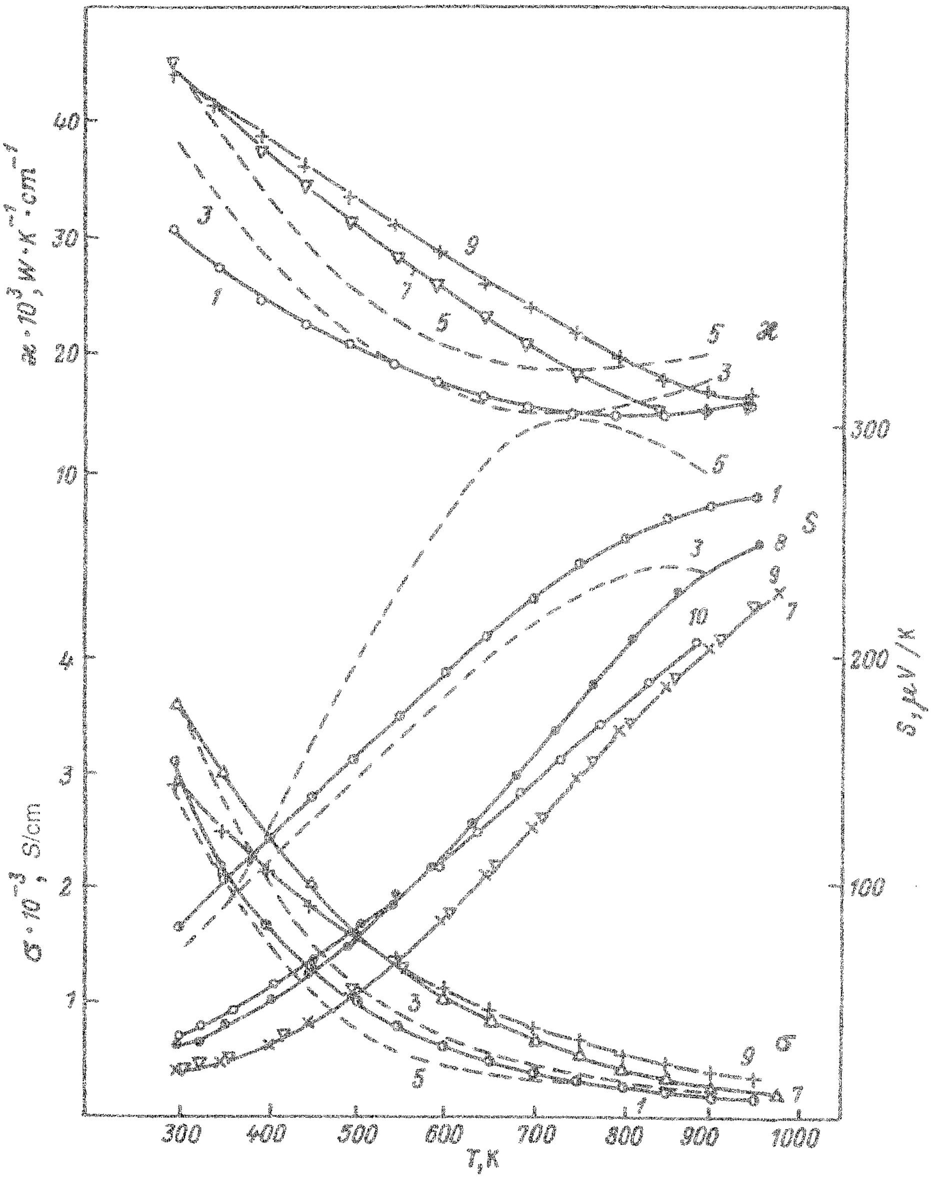

FIG. 1. Temperature dependence of the thermoelectric coefficient (S), the electrical conductivity (σ), and the thermoconductivity ($\varkappa$). The numbers on the curves correspond to sample labels in Table I.

A comparison of the thermoelectric properties of p-type PbSe and PbTe gives different results. The increase of thermoelectric power with temperature in strongly p-doped samples of PbTe(Na) (curve 5, Fig. 1) is considerably more significant than in n-type material, which explains the high values of Z for this material at 600–800 K (Fig. 2). In p-PbSe (7) this effect is much less pronounced; accordingly, the value of Z is smaller. In order to increase the thermoelectric power of strongly doped samples of p-PbSe, we attempted to change the mechanism for dissolving the acceptor-containing additive compound NaSe by isovalent doping, thereby creating conditions for the formation not only of centers for generation of free holes, but also centers for localization with resonance levels that efficiently scatter carriers with low energies.[4] Here we had in mind the results of Ref. 5 regarding the behavior of small additions of Sn to PbTe(Na). We introduced the substitutional impurities Cd and Mn into PbTe(Na) at concentrations of 1–5 at. %. Although stabilization of the Hall concentration was not observed, the thermoelectric power did increase. This latter re-

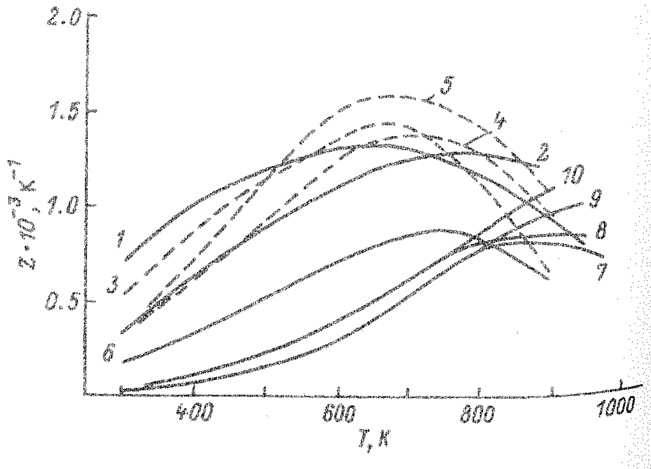

FIG. 2. Temperature dependence of the thermoelectric figure of merit Z. The numbers on the curves correspond to sample labels in Table I.

sult is illustrated by the experimental curves in Fig. 1 for PbSe with 3 at. % Cd (a) and again for the pair of samples with 2 at. % Na, along with an additional 1 at. % Mn (9) and 5 at. % Cd (10). For all these samples, the values of S did not drop below the curve (7) for PbSe. With the increase in S we noted a decrease in mobility, especially at low temperatures. Heating suppresses this effect, so that at high temperatures the ratio of values of σ in samples with different compositions is determined primarily by the ratio of their hole concentrations, i.e., the concentration of Na. The changes in Z caused by isovalent doping can primarily be traced to the increase in the thermoelectric coefficient. Thus, the thermoelectric figure of merit of sample 8 is higher than in sample 7 over the entire temperature interval. The sample of Pb(Mn)/Se (9), with its high concentration of Na, has the same thermoelectric coefficient as in sample (7); however, it exhibits higher values of Z when $T > 850$ K because its electrical conductivity is higher, due to an increased concentration of holes. Finally, the largest gain in Z is observed in the sample strongly doped with Cd (10): the increase in S and the decrease in σ, which is not so strong due to the higher level of Na doping, lead to a higher value of Z for all T. The optimum combination of properties can be expected for compositions with 1.5–2 at. % Na and 2–3 at. % Mn or Cd.

As a thermoelectric material, PbSe is cheaper and operates at a higher temperature than PbTe and GeTe. When used in a high-temperature cascade of thermoelectric batteries, the efficiency of PbSe-based thermoelectric elements is 4.7% in the temperature range 700–900 K.

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