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Thermophysical Properties of Polycrystalline PbS, PbSe, and PbTe in the Temperature Range 300–700 K

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Thermal properties (thermal conductivity λ, thermal diffusivity a, and specific heat capacity c_p of polycrystalline PbS, PbSe, and PbTe were measured in the temperature range 300–700 K. The electrical conductivity was also measured for the three substances. Lattice, electronic and bipolar components of thermal conductivity are much larger than the electronic part. The specific heat capacity is observed to increase slightly with temperature.

KEY WORDS: electrical conductivity; heat capacity; lead chalcogenides; thermal conductivity; thermal diffusivity.

1. INTRODUCTION

In recent years, a great amount of work has been done in measuring the thermal and electrical properties of the semiconducting lead chalcogenides [1–6]. However, only a limited amount of measurements are reported in the literature at temperatures above 300 K. Devyatkova and Smirnov [2] measured the thermal conductivity of a series of PbTe samples at temperatures between 80 and 450 K, and Rasulov and Medzhidov [6] measured the heat capacity of PbSe in the temperature range 300–1480 K. The present work is concerned with thermal conductivity, thermal diffusivity, specific heat capacity, and electrical conductivity of polycrystalline PbS, PbSe, and PbTe samples. The mechanism of heat transfer by phonons, electrons, bipolars, and photons is investigated. However, previous measurements of thermal conductivity showed no indication of bipolar thermal conductivity.

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Fedorov and Machuev [1] pointed out the dependence of thermal conductivity of PbTe on temperature.

2. EXPERIMENTAL PROCEDURE

PBS, PbSe, and PbTe samples were prepared by melting stoichiometric amounts of pure components in evacuated quartz ampules. The phase homogeneity of polycrystalline samples obtained was determined by X-ray structural analysis. Discs of 0.01 m diameter and 2×10^{-3} m thickness were pressed under a pressure of 15 tons $\cdot$ cm^{-2}. The calculated densities were 7550 kg $\cdot$ m^{-3} for PbS, 8050 kg $\cdot$ m^{-3} for PbSe, and 8100 kg $\cdot$ m^{-3} for PbTe. For the simultaneous determination of thermal properties (c_p, a, λ), a plane temperature waves method was used [7, 8]. The experimental errors of these properties did not exceed 3.5% for specific heat capacity and thermal conductivity, and 3–6% for thermal diffusivity measurements.

3. RESULTS AND DISCUSSION

Figure 1 shows the variation of total thermal conductivity λ_t of polycrystalline PbS, PbSe, and PbTe samples with temperature. It was

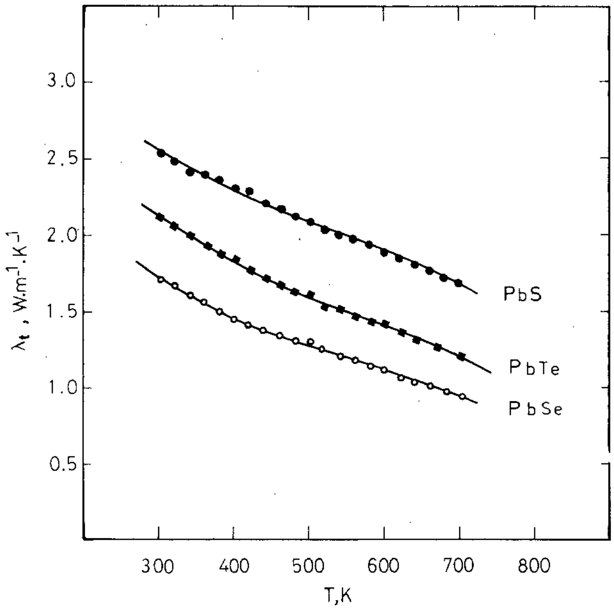

Fig. 1. Variation of the total thermal conductivity λ_t of polycrystalline PbS, PbSe, and PbTe with temperature.

found that thermal conductivity decreases as the temperature increases. The total thermal conductivity of lead chalcogenides represents the transport of heat by phonons, λ_1, free electrons, λ_e, and diffusion of electron-hole pairs (bipolars), λ_{bi}. The value of λ_e can be calculated using the Wiedemann–Franz law:

$$\lambda_e = L_0 \sigma T$$

where L_0 is the Lorenz number, and σ is the electrical conductivity. Devyatkova and Smirnov [2] showed that the calculation of λ_e is complicated due to the fact that the exact value of L_0 is not always known, but at high temperatures when degeneracy is absent while high energy electrons

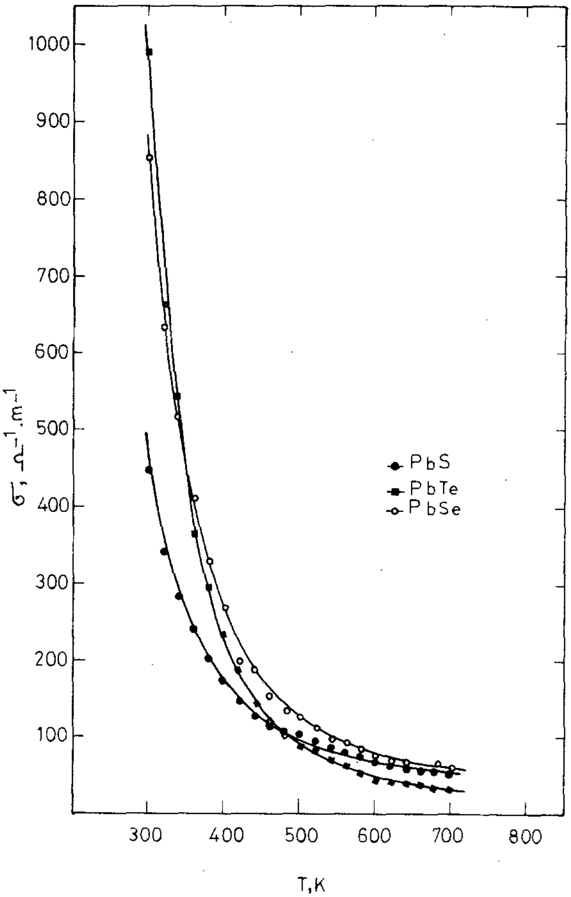

Fig. 2. Variation of the electrical conductivity of PbS, PbSe, and PbTe with temperature.

are present, the theoretical value of the Lorenz number ($L_0 = (\pi^2/3)(k/e)^2$, where k is the Boltzmann contant) can be used. Also, Muzhdaba and Shaylt [9] showed that the Lorenz number is constant at high temperatures, i.e., scattering is elastic throughout the investigated temperature range.

The measured experimental values of the electrical conductivity σ of the investigated materials are shown in Fig. 2. Electrical conductivity decreases as temperature increases, displaying a metallike impurity conduction in the investigated temperature range (300–700 K). The behavior of σ in terms of T shows that the energy required to excite the charge carriers from the impurity level is very small. The relation between $\log\sigma$ and $1/T$ is nearly linear. This means that conduction is in the intrinsic region where the carrier concentration is constant. At high temperatures, the lattice scattering becomes predominant, and resistivity tends to increase with temperature. This shows a partially metallic behavior of PbS, PbSe, and PbTe polycrystalline samples.

Table I shows the calculated value of the activation energy E_g of the three samples under consideration. The estimated value of λ_e is shown in Tables II, III, and IV for PbS, PbSe, and PbTe, respectively. The bipolar part of the thermal conductivity λ_{bi} was calculated using the following equation [10]:

$$\lambda_{bi} = \frac{3}{4}\frac{L_0 \sigma T}{\pi^2}\left(\frac{E_g}{kT} + 4\right)^2$$

The estimated values of λ_{bi} as a function of temperature for the investigated samples are also shown in Tables II, III, and IV. From the tables, it may be noted that λ_{bi} plays a greater role than the electronic part in the temperature range investigated. The lattice thermal conductivity λ_l was determined from

$$\lambda_l = \lambda_t - \lambda_e - \lambda_{bi}$$

It was found the λ_l decreases with temperature. The mechanism of heat transfer by photons was calculated for the three substances using the data

Table I. Activation Energy of PbS, PbSe, and PbTe

Substance	E_g (eV)
Pbs	0.194
PbSe	0.296
PbTe	0.316

Table II. Electrical and Thermal Properties of PbS

T (K)	σ $(\Omega^{-1} \cdot m^{-1})$	c_p $(J \cdot kg^{-1} \cdot K^{-1})$	a $(10^{-5}\,m^2 \cdot s^{-1})$	λ_t $(W \cdot m^{-1} \cdot K^{-1})$	λ_e $(10^{-3}\,W \cdot m^{-1} \cdot K^{-1})$	λ_{bi} $(10^{-3}\,W \cdot m^{-1} \cdot K^{-1})$	λ_l $(W \cdot m^{-1} \cdot K^{-1})$
300	445.80	2.85	11.80	2.539	3.277	32.94	2.503
320	340.40	3.00	11.00	2.492	2.669	24.68	2.465
340	284.30	3.05	10.70	2.464	2.368	20.29	2.441
360	244.70	3.12	10.20	2.403	2.158	17.23	2.384
380	200.30	3.25	9.59	2.353	1.865	13.95	2.337
400	172.40	3.29	9.30	2.310	1.690	11.90	2.296
420	148.40	3.34	9.08	2.290	1.527	10.16	2.278
440	127.70	3.40	8.65	2.220	1.377	8.69	2.210
460	115.60	3.45	8.36	2.178	1.303	7.83	2.169
480	108.80	3.51	8.07	2.139	1.280	7.34	2.130
500	104.60	3.56	7.84	2.107	1.281	7.03	2.099
520	91.80	3.59	7.55	2.046	1.170	6.17	2.039
540	85.60	3.60	7.38	2.006	1.132	5.74	1.999
560	81.45	3.63	7.17	1.965	1.117	5.46	1.958
580	73.70	3.65	6.99	1.926	1.047	4.94	1.920
600	66.70	3.68	6.79	1.887	0.980	4.47	1.882
620	63.40	3.71	6.58	1.843	0.963	4.26	1.838
640	60.30	3.74	6.39	1.804	0.946	4.06	1.799
660	57.40	3.75	6.23	1.764	0.928	3.87	1.759
680	54.60	3.75	6.04	1.710	0.910	3.69	1.705
700	51.93	3.78	5.87	1.675	0.891	3.52	1.671

Table III. Electrical and Thermal Properties of PbSe

T (K)	σ ($\Omega^{-1} \cdot m^{-1}$)	c_p ($J \cdot kg^{-1} \cdot K^{-1}$)	a ($10^{-5}\ m^2 \cdot s^{-1}$)	λ_t ($W \cdot m^{-1} \cdot K^{-1}$)	λ_e ($10^{-3}\ W \cdot m^{-1} \cdot K^{-1}$)	λ_{bi} ($10^{-3}\ W \cdot m^{-1} \cdot K^{-1}$)	λ_l ($W \cdot m^{-1} \cdot K^{-1}$)
300	854.10	2.80	7.71	1.738	6.28	113.97	1.618
320	632.70	2.90	6.96	1.625	4.96	81.62	1.538
340	518.00	3.00	6.60	1.594	4.30	64.82	1.525
360	403.40	3.05	6.28	1.542	3.56	49.48	1.489
380	330.30	3.07	6.12	1.512	3.08	39.70	1.469
400	270.40	3.10	5.86	1.462	2.65	31.83	1.428
420	200.30	3.15	5.67	1.438	2.06	23.16	1.413
440	190.60	3.20	5.42	1.396	2.05	21.67	1.372
460	156.00	3.23	5.28	1.373	1.76	17.55	1.354
480	134.30	3.25	5.08	1.329	1.58	14.91	1.313
500	127.70	3.26	4.98	1.307	1.56	13.98	1.291
520	115.60	3.26	4.82	1.265	1.47	12.54	1.251
540	99.50	3.25	4.67	1.222	1.32	19.74	1.210
560	94.50	3.30	4.39	1.166	1.30	10.12	1.155
580	85.60	3.30	4.33	1.150	1.22	9.11	1.140
600	73.70	3.33	4.23	1.134	1.08	7.75	1.125
620	70.10	3.32	4.16	1.112	1.06	7.32	1.104
640	66.60	3.35	3.97	1.071	1.04	6.92	1.063
660	63.40	3.35	3.81	1.027	1.03	6.62	1.019
680	64.60	3.38	3.69	1.004	0.90	5.59	0.998
700	50.90	3.40	3.60	0.985	0.87	5.24	0.979

Table IV. Electrical and Thermal Properties of PbTe

T (K)	σ ($\Omega^{-1} \cdot m^{-1}$)	c_p ($J \cdot kg^{-1} \cdot K^{-1}$)	a ($10^{-5}\ m^2 \cdot s^{-1}$)	λ_t ($W \cdot m^{-1} \cdot K^{-1}$)	λ_e ($10^{-3}\ W \cdot m^{-1} \cdot K^{-1}$)	λ_{bi} ($10^{-3}\ W \cdot m^{-1} \cdot K^{-1}$)	λ_l ($W \cdot m^{-1} \cdot K^{-1}$)
300	992.40	3.00	8.81	2.141	7.29	145.63	1.988
320	665.10	3.15	8.14	2.077	5.21	94.51	1.977
340	455.60	3.24	7.70	2.021	4.54	75.33	1.941
360	365.10	3.35	7.10	1.927	3.22	49.19	1.875
380	298.85	3.46	6.77	1.897	2.78	39.32	1.855
400	232.70	3.51	6.51	1.851	2.28	30.01	1.819
420	190.60	3.57	6.22	1.799	1.96	24.11	1.773
440	148.40	3.64	5.93	1.748	1.60	18.48	1.728
460	121.50	3.70	5.68	1.702	1.37	14.91	1.686
480	104.60	3.76	5.55	1.690	1.23	12.65	1.676
500	90.00	3.81	5.25	1.620	1.10	10.73	1.608
520	85.60	3.84	5.08	1.580	1.09	10.11	1.569
540	77.47	3.90	4.96	1.567	1.03	9.10	1.557
560	63.40	3.93	4.67	1.487	0.87	7.35	1.479
580	57.40	3.97	4.57	1.470	0.82	6.63	1.463
600	47.00	4.00	4.40	1.426	0.69	5.36	1.420
620	44.70	4.03	4.24	1.384	0.68	5.07	1.378
640	42.50	4.06	4.08	1.342	0.67	4.82	1.337
660	40.80	4.06	3.95	1.299	0.66	4.58	1.294
680	38.50	4.10	3.79	1.259	0.64	4.29	1.254
700	36.60	4.10	3.65	1.212	0.63	4.08	1.207

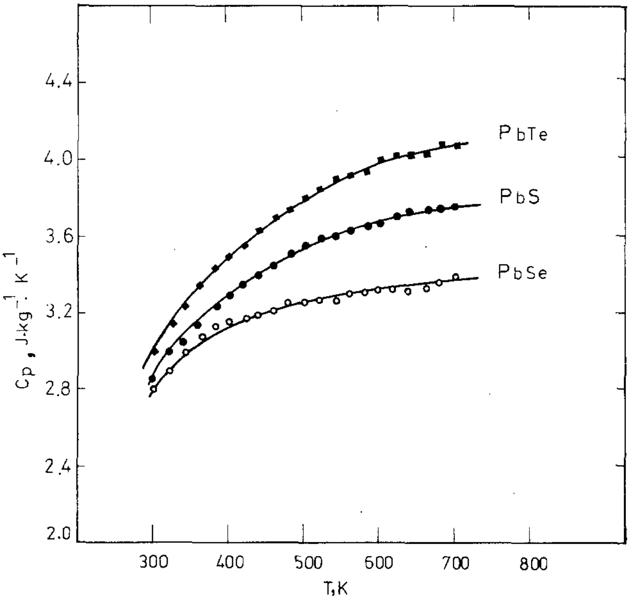

Fig. 3. Variation of the specific heat capacity of PbS, PbSe, and PbTe with temperature.

reported for the absorption coefficient [11] and data reported for the refractive index [12].

The calculated value of thermal conductivity due to photons at 300 K is equal to 4×10^{-5}, 4.5×10^{-5}, and 6×10^{-5} $\mathrm{W \cdot m^{-1} \cdot K^{-1}}$ for PbS, PbSe, and PbTe, respectively. The radiative part of the thermal conductivity is quite negligible. The mechanism of heat transfer can be summarized as follows. For PbS, it is 98.6% phonons, 1.2% bipolars, and 0.12% electrons. For PbSe, it is 92.8% phonons, 6.5% bipolars, and 0.36% electrons. For PbTe, it is 92.8% phonons, 6.8% bipolars, and 0.34% electrons at 300 K.

Thermal diffusivity data are listed in Tables II, III, and IV. Figure 3 shows the variation of c_p with temperature for PbS, PbSe, and PbTe. The specific heat capacity increases slightly with temperature. It is possible that anharmonicity and increase in conduction electrons and electronic heat capacity are responsible for the increase in c_p.

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