Thermal conductivity of CsBi alloy in liquid state

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Abstract. Experimental data on the thermal conductivity and thermal diffusivity of a liquid alloy CsBi of the equiatomic composition in the temperature range from the liquidus line to 1173 K have been obtained. The measurements were carried out on the basis of the laser flash method using a sealed steel cell. For studied properties the approximation equations and a table of recommended values are presented. The analysis of the obtained results confirms the existing assumption about liquid cesium-bismuth alloys as associated solutions.

1. Introduction
Liquid alloys of the alkali metal-bismuth type belong to a unique and poorly studied class of so-called ion-metal melts, which possess a number of specific physicochemical properties [1–3]. The molar volume concentration dependence of these liquid systems demonstrates strong deviations from that for ideal solutions, and near some concentrations there are electrical resistance peaks, which are 15–40 times higher than the electrical resistance of pure liquid bismuth [4, 5]. These anomalies are explained by the fact that the components of these systems differ greatly in electronegativity so that, in addition to the metal type of interatomic interaction, there is a tendency to form an ionic (or ion-covalent) bond. This leads to the formation of intermetallic complexes in melts with a partially ionic character of interatomic interaction [3, 5]. The existence of such complexes in melts is confirmed only by indirect experimental data. The development of theoretical assumption about the structure of liquid alkali bismuthides is restrained, in particular, due to the lack of experimental information about their thermophysical properties including transport properties. According to our information, the thermal conductivity of liquid alkali metal-bismuth alloys has not yet been measured.

The purpose of this work was to experimentally study the coefficients of thermal conductivity ($\lambda$) and thermal diffusivity ($a$) of the CsBi alloy with equiatomic composition in a wide temperature range of the liquid state.

2. Experimental technique
The thermal conductivity coefficient of the liquid cesium-bismuth alloy (50 at. % Bi) was studied by the laser flash method. The experimental setup and measurement technique are described in [6, 7] in detail. A measuring cell of 12Kh18N10T stainless steel with special geometry was used, in which a liquid sample was “clamped” between the crucible and the lid, forming a flat layer of 2.4 mm thickness. The cesium and bismuth used for the preparation of the alloy had a purity of 99.94 and 99.98 wt. %, respectively. The alloy preparation was carried out in a glovebox filled with pure argon (99.992% by volume). The surfaces of metal ingots were preliminarily mechanically cleared from oxide films and nitrides. The weights of Cs and Bi pieces needed to calculate the equiatomic
composition were determined on an analytical balance with an accuracy of 2–3 mg, taking into account “the effect of chemical contraction” [2] between these metals. The mass of the composite sample in the cell was 4.3 g. The actual Bi content in the studied alloy was 49.95 ± 0.03 at. %. The sealing of the cell was performed by arc welding directly in the inert atmosphere of the glovebox.

Before the experiments the cell was installed in a setup furnace, which was then evacuated and filled with argon up to 0.1 MPa pressure. The sample at the maximum temperature of the experiment was kept in the liquid state for some time for homogenizing. It should be noted that the small mass of the sample in the cell and the chemical reaction between liquid bismuth and cesium [2, 8] ensured the homogeneity of the alloy in composition. The measurements were taken in the cooling mode from a temperature of 1173 K to a solid state. The reproducibility of the results in different thermal cycles confirmed the chemical inertness of stainless steel to the liquid CsBi alloy.

The processing of primary data was carried out on a three-layer model (crucible – melt – lid) based on the developed software package [6, 7]. The two-dimensional heat equation was solved in cylindrical coordinates. In the calculations, we used the given values of the cell material properties, as well as the density (ρ) and heat capacity (c_p) of the melt alloy. Fitting parameters for the calculation were the thermal conductivity of the melt and the emissivity of the external surfaces of the cell. The emissivity was actually an effective value responsible for all heat loss of the cell, including conductive and convective heat transfer in the surrounding gas medium. The data on ρ and c_p of the studied alloy had been obtained before by the gamma-ray attenuation technique [8] and isoperibol drop calorimetry [9] with an accuracy of 0.4 and 1.5%, respectively. The change in the melt layer thickness as taken into account through the thermal expansion of the cell material. The error in measuring the thermal conductivity of a liquid alloy was 4–6% depending on the temperature. The magnitude of this error was mainly due to the uncertainty of the cell material properties, as well as the error of heat capacity of the studied alloy [6, 7].

### 3. Results and discussion

The measurement results of thermal conductivity λ of liquid CsBi alloy in the temperature interval 670–1173 K are presented in Figure 1. The graph also contains data on the thermal conductivity of the fluoride molten salt FLiNaK [10] and the values of λ_{id} for an ideal solution (λ_{id} = 0.5λ_C + 0.5λ_Bi). Data for λ_C and λ_Bi were taken from [11, 12]. Thermal conductivity of high temperature FLiNaK was determined also by laser flash technique. For measurements in [10] a special designed graphite crucible was used. As can be seen from Figure 1, CsBi alloy has the low thermal conductivity values typical of liquid salts [10] and its λ is an order of magnitude smaller than the value of λ_{id}, which confirms the existing assumptions [3, 5] about intermetallic complexes in alkali metal-bismuth type liquid alloys.

The approximation of the obtained results from the temperature by the least squares method has given the following equation:

\[
λ(T) = -0.023 + 0.002 T - 2.419 \times 10^{-7} T^2,
\]

where λ is in W/(m K), T is in K. The standard deviation of the experimental points from (1) does not exceed 1.4%.

According to the measurement results of λ and the literature data for ρ and c_p, the thermal diffusivity coefficient (a) of the alloy was calculated by the formula:

\[
a = \frac{λ}{ρ c_p}.
\]

The approximation equation for a in the same temperature range as for λ has the form:

\[
a(T) = 0.096 + 8.381 \times 10^{-4} T + 6.254 \times 10^{-7} T^2,
\]

where a is in mm^2/s. The standard deviation of the calculated points from (3) does not exceed 1.3%. The error in determining a by formula (2) practically coincides with the error of λ, since they differ in
a known multiplier $\rho c_p$. The data of $\rho$ and $c_p$ have been used in determining $\lambda$, therefore their uncertainties already are included in the overall error in the $\lambda$.

![Graph](image)

**Figure 1.** The thermal conductivity of the liquid alloy CsBi (50 at. % Bi).
1 – our experimental data, 2 – equation (1), 3 – $\lambda$ data of the fluoride molten salt FLiNaK [10], 4 – $\lambda_{id}$ values for an ideal solution ($\lambda_{id} = 0.5\lambda_{Cs} + 0.5\lambda_{Bi}$).

Table 1 shows the smoothed values of $\lambda$ and $\alpha$ with their errors.

| $T$, K | $\lambda$, W/(m K) | $\alpha$, mm$^2$/s | $\delta\lambda$, $\delta\alpha$, % |
|--------|---------------------|---------------------|----------------------------------|
| 670    | 1.20                | 0.94                | 4                                |
| 700    | 1.25                | 0.99                | 4                                |
| 800    | 1.41                | 1.17                | 5                                |
| 900    | 1.57                | 1.36                | 5                                |
| 1000   | 1.72                | 1.56                | 5                                |
| 1100   | 1.87                | 1.77                | 6                                |
| 1173   | 1.98                | 1.94                | 6                                |

**Conclusion**

The thermal conductivity of alkali metal-bismuth type alloy was measured for the first time. New experimental data on $\lambda$ and $\alpha$ for liquid CsBi of the equiatomic composition in the temperature range from the liquidus line to 1173 K with an error of 4–6% have been obtained. It is shown that the alloy has low $\lambda$ values typical of molten salts and its $\lambda$ is an order of magnitude smaller than the thermal conductivity calculated according to the additivity rule.
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