ELEKTROPHYSICAL PROPERTIES OF $ErSbSe_3$ AND $ErBiSe_3$ COMPOUNDS

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In the present paper, the specific electrical conductivity of $ErSbSe_3$ and $ErBiSe_3$ compounds in the temperature range of 300÷900 K, thermoEMF, temperature dependences of the thermoelectric coefficient, and total thermal conductivity were studied. It was determined that both compounds have a complex zone structure. It has been established that the bipolar mechanism of thermal conductivity has a strong effect on the temperature dependence of the thermal conductivity of the $ErBiSe_3$ compound. In addition, calculations of the values of the thermoelectric efficiency coefficient of the $ErBiSe_3$ compound have shown that the compound is promising to fabricate the negative arm of thermocouples.

The specific electrical conductivity of the $ErBiSe_3$ compound decreases slightly in the temperature range of 300-540K and has a semimetallic character. At temperatures above 600K, this increase becomes sharper and has a linear character. The value of the thermo-e.h.q. coefficient reaches a maximum at 700K, and then decreases, i.e. its temperature-dependent change is complex.

Analogous processes From the temperature dependence of the thermoelectric coefficient of the $ErSbSe_3$ compound, it was found that the $ErBiSe_3$ and $ErSbSe_3$ compounds have “n”-type conductivity. The $ErBiSe_3$ compound can be used as a promising thermoelectric material in the preparation of thermoelectric energy converters.

Keywords: ternary compound, kinetic coefficients, complex zone structure, thermoelectric efficiency, negative arm of the thermocouple.
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INTRODUCTION

Complex chalcogenides of heavy metals and phases based on them have long attracted the attention of researchers due to their promising functional properties [1-5]. Among the materials listed, compounds of the B_2X_3(B^V – Sb, Bi; X – Se, Te) type occupy a special place due to their interesting properties [6-10]. The introduction of lanthanide atoms into the crystal lattice of such compounds can improve their properties and create additional functionality [11-15].

In order to optimize the properties of functional compounds, it is important to develop the physicochemical basis for the synthesis of new inorganic functional materials, which is possible based on studying the phase diagrams of the corresponding systems [16-19].

Compounds $ErSbSe_3$ and $ErBiSe_3$ are formed in the Er_2Se_3-Sb_2Se_3 and Er_2Se_3-Bi_2Se_3 systems. These compounds melt with decomposition according to peritectic reactions at 850 and 1100 K and crystallize in the orthorhombic syngony with the unit cell parameters a=12.49, b=14.55, c=5.82 Å ($ErSbSe_3$) and a=12.68, b=14.30, c=5.15 Å, ($ErBiSe_3$) [20].

This article continues the study of these compounds and presents the results of determining the number of their physical properties, namely, the specific electrical conductivity, thermoEMF, temperature dependences of the coefficient termoEMF and total thermal conductivity of $ErSbSe_3$ and $ErBiSe_3$ compounds in the temperature range of 300÷900 K,

At the same time, the degree of suitability of these compounds for thermoelectric energy sources is determined.

EXPERIMENTAL PART

The samples were synthesized from elementary components (Er, powder, CAS № 7440-52-0; Sb, powder, 7440-36-0; Bi; powder, 7440-69-9; Se, powder, 7782-49-2). For this purpose, pre-calculated samples were weighed on an analytical scale with an accuracy of 0.0001, filled into quartz ampoules, evacuated to 10^{-3} Pa, and soldered in an oxygen-gas flame. Then, the samples were synthesized at a temperature of 1200K in one-temperature vertical furnaces. The synthesized samples were thermally treated for 250 h. at a temperature 50-100 K lower than the solidus to obtain homogeneous equilibrium samples.

To study the electrophysical properties, the synthesized $ErSbSe_3$ and $ErBiSe_3$ compounds were annealed for 300 h. at a temperature of 550-600 ^{0}C and then pressed into a cylindrical form. The thermoelectric coefficient (α), specific electrical conductivity (σ), and total thermal conductivity (χ) were measured.

The measurements of thermoelectric coefficient (α) and specific electrical conductivity (σ) were performed according to the methodology using the compensation method [21]. The total thermal conductivity was measured by the stationary method [22]. Specific electrical conductivity and thermoEMF measurement errors were about 3-5%, and the measurements of the total thermal conductivity were performed with an error of 5-7%.

RESULTS AND DISCUSSIONS

The specific electrical conductivity of the $ErBiSe_3$ compound and the temperature dependence of the termoEMF coefficient are given in Figure 1. The

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electrical conductivity decreases relatively weakly in the temperature range of 300 – 540 K, and the conductivity is semimetallic.

Starting from ~T ≥ 560 K, the electrical conductivity increases with increasing temperature. At values of ~T≥ 600 K, such an increase becomes sharper according to the straight-line law. It can be assumed that the last temperature interval corresponds to the field of specific conductivity. From this part, the band gap was calculated for the studied compounds and the obtained value was ~ 0.16eV.

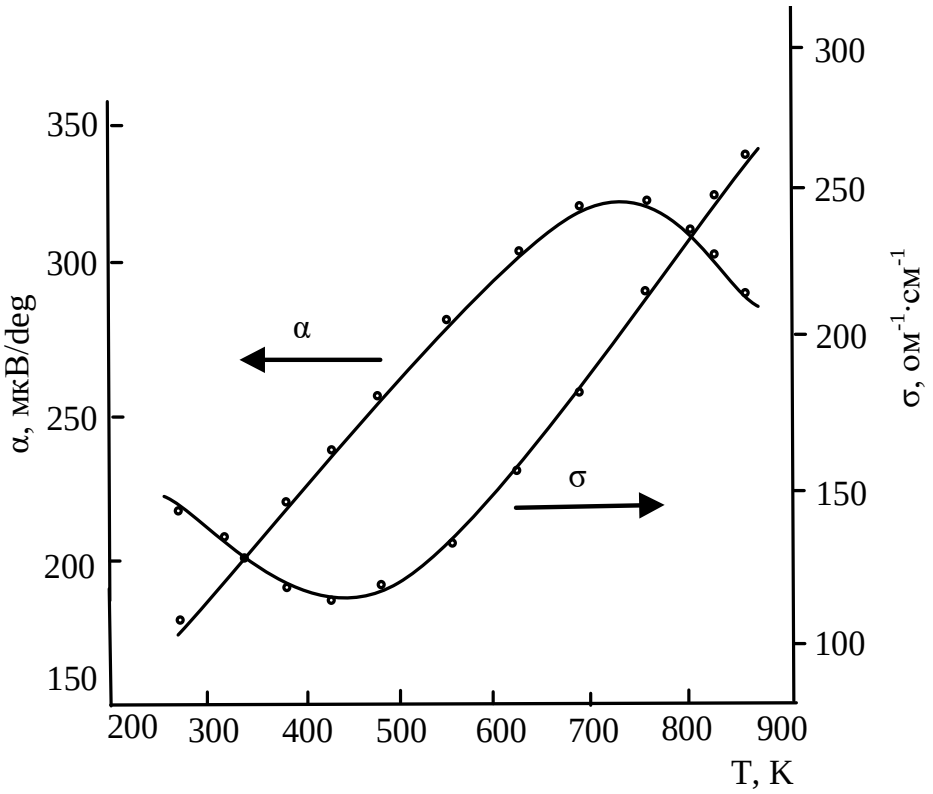

Fig. 1. The temperature dependences of the specific electrical conductivity (σ) and thermo-e.m.f. coefficient (α) of the $ErBiSe_3$ compound.

The value of the thermoEMF coefficient depends on temperature, at first it is insignificant (~T≤ 410 K), and then increases sharply, and at a temperature T = 700 K the thermo-EMF coefficient takes on its maximum value. With a subsequent increase in temperature (~T>710 K) the value of α tends to decrease. As can be seen, thermoEMF has a complex character depending on temperature.

Typically, such a change in the therm EMF coefficient with increasing temperature is observed in materials with a complex band structure. Thus, according to the literature, the valence bands of such materials consist of one or more half-bands, and the charge carriers in these half-bands are strongly affected by temperature [23]. However, at relatively low temperatures, the charge carriers become passive and have little effect on the kinetic coefficients.

As a result, the compound behaves as a material with a simple band structure, and the thermoEMF coefficient has a weak linear change. With increasing temperature, charge carriers in the other half-band are activated, which leads to the thermoEMF coefficient increasing more and reaching its maximum. After the activity of the charge carriers in the other half-bands weakens, that is, after the maximum is observed in α~f (T) dependence, the thermoEMF coefficient decreases

Another reason for the decrease in the coefficient at high temperatures may be the absence of a specific conductivity field in the sample. Similar thermo EMF processes are also observed in the temperature dependence of the coefficient of the $ErSbSe_3$ compound (Figure 2). It is assumed that both compounds have a complex band structure.

From the temperature dependences of the thermo EMF coefficient, it can be seen that they have n-type conductivity. The second graph in Figure 2 shows the temperature dependence of the specific electrical conductivity of the $ErSbSe_3$ compound. Here, semi-metallic conductivity is observed up to ~500 K. According to the dependence trend in this region, the value of the band gap was (~0.19 eV). The change in electrical conductivity at low temperatures (in the range of 300-600 K) is semi-metallic.

Figure 3 shows the temperature dependencies of the total thermal conductivity of the $ErBiSe_3$ and $ErSbSe_3$ compounds. For the $ErSbSe_3$ compound the χ~f(T) dependence obeys the T^{-1} law over the entire temperature range, while for the $ErBiSe_3$ compound above ~600 K, this law is violated.

That is, in the range of ~600÷673 K, the total thermal conductivity tends to increase.

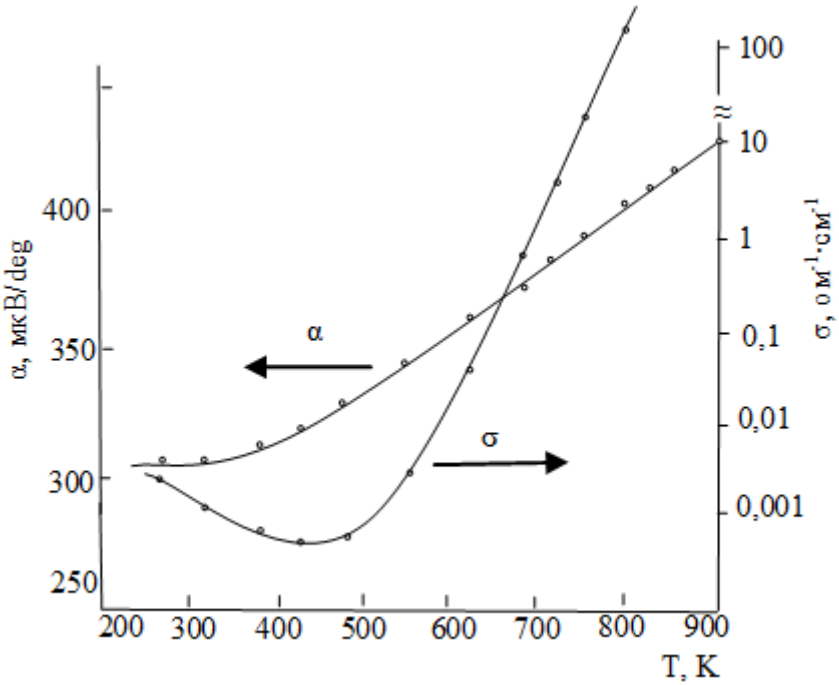

Fig. 2. The temperature dependencies of the specific electrical conductivity (σ) and thermo-e.m.f. coefficient (α) of the $ErSbSe_3$ compound.

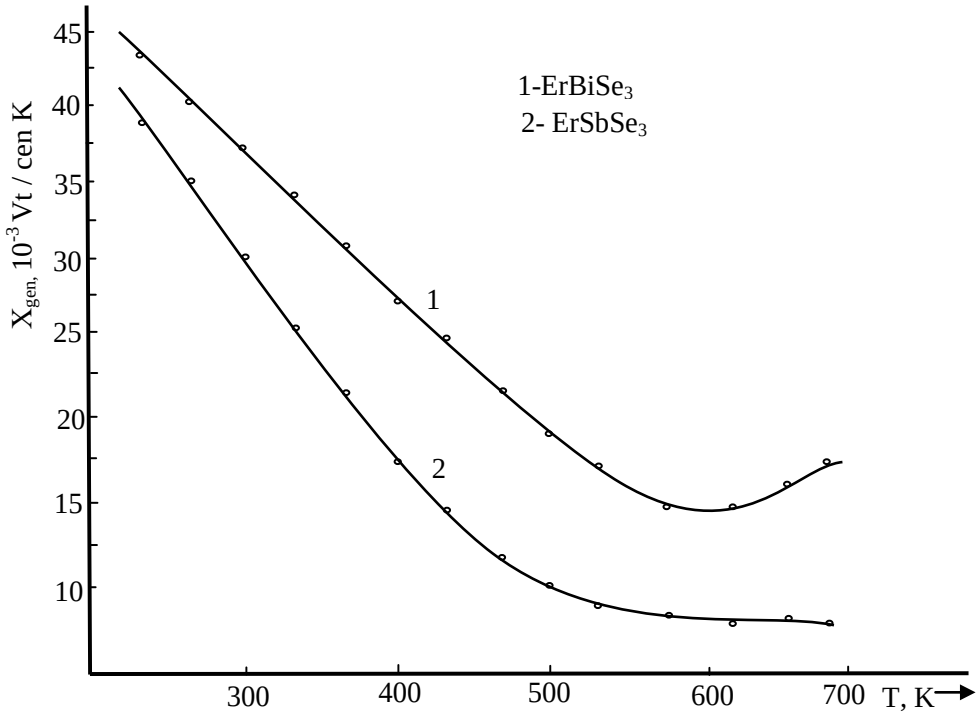

Fig. 3. Temperature dependence of the total thermal conductivity of $ErBiSe_3$ and $ErSbSe_3$ compounds

Usually, the increase in thermal conductivity at high temperatures is associated with the formation of bipolar thermal conductivity [24]. To clarify this mechanism in the studied $ErBiSe_3$ compound, the total thermal conductivity (χ) [25]. was calculated using the following relation

$$\chi = 2\,L\sigma T\left(\frac{\Delta E}{kT} + 1\right),$$

where L is the Lorentz number, which is also taken to be 1.48×10^{-8} according to [26].

Figure 4 shows the temperature dependence of the total thermal conductivity for the $ErBiSe_3$ compound. As can be seen, total thermal conductivity increases with increasing temperature, and its values are quite high. That is, it can be considered that the effect of this quantity at high temperatures is noticeable.

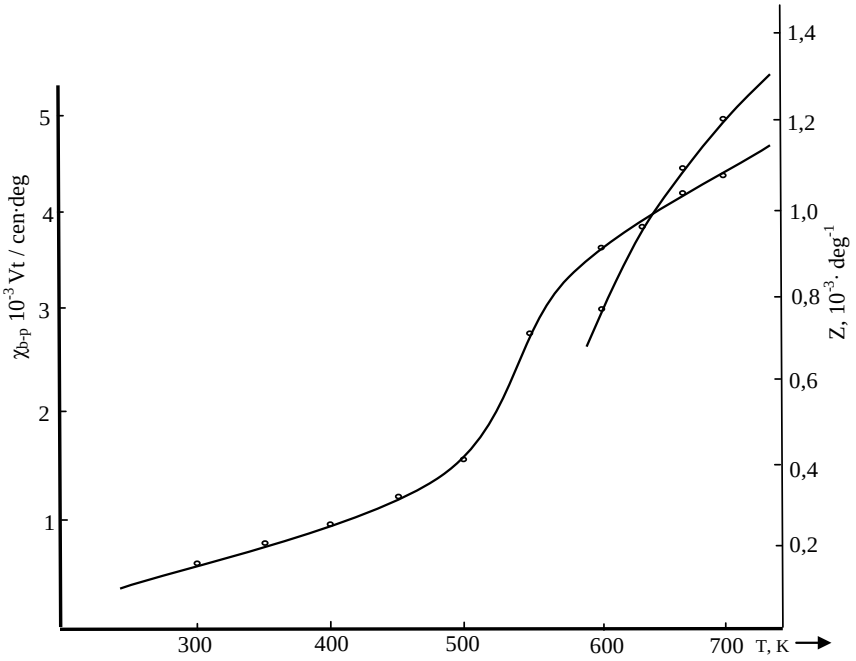

Fig. 4. Variation of bipolar thermal conductivity (χ_{bp}) and thermoelectric efficiency (Z) of $ErBiSe_3$ compound as a function of temperature.

Taking into account the high values of the kinetic coefficients (α and σ) of the $ErBiSe_3$ compound, the values of its thermoelectric efficiency (Z) were calculated at different temperatures.

The second graph in Figure 4 shows the temperature dependence of the thermoelectric efficiency of the $ErBiSe_3$ compound. Although at relatively low temperatures the Z value is not very large, above ~600 K the value of the thermoelectric efficiency coefficient becomes greater than unity. This indicator is an effective indicator of the suitability of the compound as a negative arm of a thermocouple.

CONCLUSION

Thus, the work studied the thermoelectric properties of the $ErSbSe_3$ and $ErBiSe_3$ compounds.

From the temperature dependences of the thermoelectric parameters of the $ErBiSe_3$ and $ErSbSe_3$ compounds, it can be concluded that these compounds have a complex band structure, and $ErBiSe_3$ can be used as a promising thermoelectric material in the manufacture of thermoelectric energy converters.

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