Dependence of the Seebeck Coefficient on Specific and Universal Electrical Conductivities of $Bi_2Sr_2Co_{1.8}O_y$ Thermoelectric Doped with Strontium Borate and Graphene

Authors' contributions

This work was carried out in collaboration between both authors. Both authors read and approved the final manuscript.

ABSTRACT

The paper considers the dependences of the Seebeck coefficient on the specific and universal electrical conductivities in $Bi_2Sr_2Co_{1.8}O_y$ thermoelectric doped with strontium borate- $Sr(BO_2)_2$ and graphene. It is shown that the dependences of the Seebeck coefficient on the electrical conductivity in the doped compositions are rectilinear for individual samples. The dependences of the Seebeck coefficient on the universal electrical conductivity exhibit a power-law character, but their form is practically independent of the dopant concentrations. The temperature dependences of the electronic quality factor (B_E) are also investigated. An increase of B_E with temperature indicates the presence of effects of additional scattering and band convergence.

Keywords: $Bi_2Sr_2Co1._8O_y$ thermoelectric, doping, electrical conductivity.

1. INTRODUCTION

Layered cobaltites are promising materials for high-temperature thermoelectric generators [1, 2]. In order to enance their functional efficiency (in particular, increase the power factor σS^2 (σ is the electrical conductivity, S is the Seebeck coefficient) doping method is widely used. Based on the data reported in [3, 4], the dependences of the Seebeck coefficient on the specific and universal electrical conductivities in $Sr(BO_2)_2$ and graphene-doped $Bi_2Sr_2Co_{1.8}O_y$ thermoelectrics were investigated in this paper.

The formula for the dependence of the Seebeck coefficient on the characteristics of charge carriers has the form [5-7]:

$$S = \frac{8\pi^2 k_B^2}{3qh^2} m^* T \left(\frac{\pi}{3n}\right)^{2/3}, \qquad (1)$$

where n is their concentration, m* is the effective mass, q is the elementary charge, T is the absolute temperature, k_B and h are the Boltzmann and Planck constants. Taking into account

the expression for electrical conductivity σ=nqμ (μ - mobility) and the values of universal constants, formula (1) will take the form:

$$S = 2.17 \cdot 10^{-16} m^* \mu^{2/3} T \sigma^{-2/3}. \qquad (2)$$

The concept of universal electrical conductivity is also introduced:

$$\sigma' = \frac{\sigma}{B_E}\left(\frac{q}{k_B}\right)^2, \qquad (3)$$

where $B_E=\sigma S^2/B_S$ is the electronic quality factor, and B_S is a dimensionless quantity (scaled power factor) depending on the Seebeck coefficient [8]. Using Eqs.(2) and (3):

$$S = 5.7 \cdot 10^{-11} m^* \mu^{2/3} T B_E^{-2/3} (\sigma')^{-2/3} \ . \qquad (4)$$

In this paper, we consider the dependences of the Seebeck coefficient on the specific and universal electrical conductivities in $Bi_2Sr_2Co_{1.8}O_y$ thermoelectric doped with $Sr(BO_2)_2$ and graphene

2. RESULTS AND DISCUSSION

Eq.(2) rewrite as: $S=C\sigma^{-2/3}$, where $C= 2.17 * 10^{-16} m^* \mu^{2/3} T$. Study the dependence S-$\sigma^{-2/3}$ shows that the variable coefficient $C=S\sigma^{2/3}$ changes small with temperature for the samples under study.

It should be noted that the comparative narrowness of the diapazone of the change of S ((1.05-1.78)10^{-4}V·K^{-1}) makes it possible to consider the dependence of the Seebeck coefficient on the electrical conductivity for our samples in a simpler way. The study of the relationship between the power factor and the Seebeck coefficient showed that for all samples (both with a dopant and with an additive), the dependences σS^2–S are rectilinear (Fig.1):

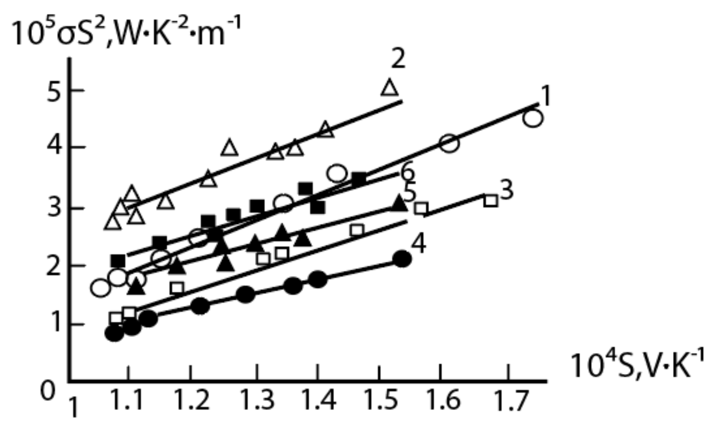

Figure 1. Dependences of the power factor on the Seebeck coefficient: $Bi_2Sr_{2-x}[Sr(BO_2)_2]_xCo_{1.8}O_y$ – (o) x=0.075, (Δ) x=0.1, (□) x=0.15; $Bi_2Sr_2Co_{1.8}O_y$+ xGr – (●) x=0.35, (▲) x=0.7, (■) x=1.15.

$$\sigma S^2=kS + b, \qquad (5)$$

where k is the slope of the lines, b is the ordinate of the point of intersection of these lines with the σ axis during their extrapolation (the values of k and b are given in the table).

Table 1: Values of constants in Eq.(5) for different x (=0.075-0.15: $Sr(BO_2)_2$, =0.35-1.15: Gr)

x	k, $Sim(K\cdot m)^{-1}V$	$10^5 b, W\cdot K^{-2}\cdot m^{-1}$
0.075	0.22	-1.3
0.1	0.5	-2.35
0.15	0.4	-2.2
0.35	0.39	-2.55
0.7	0.45	-2.8
1.15	0.3	-2

Eq.(5) is rewritten as:

$$\sigma = \frac{kS + b}{S^2} = \frac{k}{S} + \frac{b}{S^2} \qquad (6)$$

and consider the dependence S– σ in this implicit form. Graph of Eq. (6) is a curve of the 3rd order, but due to the small range of change in S, we have segments in the form of almost straight lines (Fig.2). For comparison, we plotted these dependences for larger ranges of change of S (up to (2.5-5) $\cdot 10^{-4} V\cdot K^{-1}$) for other thermoelectrics [9-11]. A deviation from straightness was observed, which follows from the above formulas.

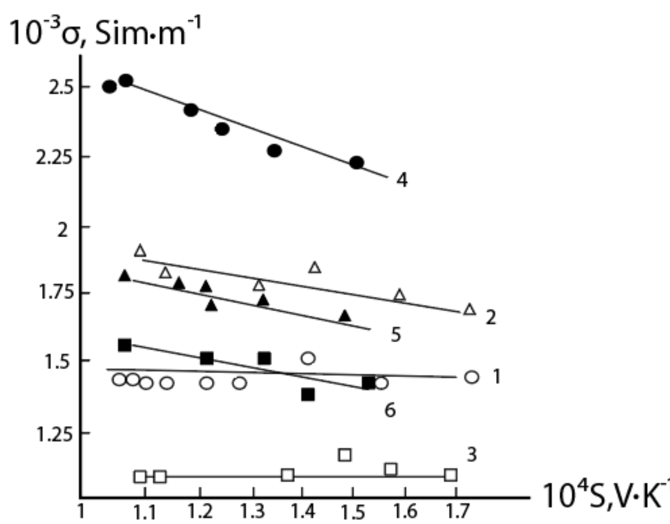

Figure 2. Implicit dependences S − σ: $Bi_2Sr_{2-x}[Sr(BO_2)_2]_xCo_{1.8}O_y$ − (o) x=0.075, (Δ) x=0.1, (□) x=0.15; $Bi_2Sr_2Co_{1.8}O_y$+ xGr − (●) x=0.35, (▲) x=0.7, (■) x=1.15.

It can be seen from Fig. 2 that for most samples, an increase in S leads to a decrease in σ (and vice versa), which also follows from the above formulas. Since σ and S depend on temperature, an increase in the latter leads to an increase in the power factor exclusively for all samples. (A study of the dependence of the power factor on σ and S separately showed

that σS^2 decreases with increasing σ and increases as S increases. And since σS^2 depends on S more than on σ, the result is an increase in the power factor.)
Eq.(4) rewrite as: $S=C'(\sigma')^{-2/3}$, where $C' = 5.7 * 10^{-11} m^* \mu^{2/3} T B_E^{-2/3}$. The coefficient C' changes small with temperature, as well as the coefficient C in the equation $S=C\sigma^{-2/3}$.
Taking $B_E=\sigma S^2/B_S$ into account, formula (3) will take the form:

$$\sigma' = \left(\frac{q}{k_B}\right)^2 \frac{B_S}{S^2} = \left(\frac{q}{k_B}\right)^2 \frac{\sigma}{B_E} \cong 1.347 * 10^8 \frac{B_S}{S^2} \quad (7)$$

or

$$S = 1.16 * 10^4 B_S^{1/2} (\sigma')^{-1/2}. \quad (8)$$

Dependences S–σ' according to the formula (8) for the studied samples are shown in Fig.3. It can be seen that the experimental points here also form almost a single set, regardless of the concentration of both the additive and the dopant (i.e. B_E scales electrical conductivity). Their combination can be described by a single empirical expression $S \cong 6.79 \cdot 10^4 (\sigma')^{-0.526} - 1.5 \cdot 10^{-5}$. (Obviously, the dependence $\sigma' - B_S/S^2$, constructed according to formula (7), will have the same form for any thermoelectric – the form of a straight line with a slope of $\cong 1.347 * 10^8$ $SimW^{-1}K^2$.)

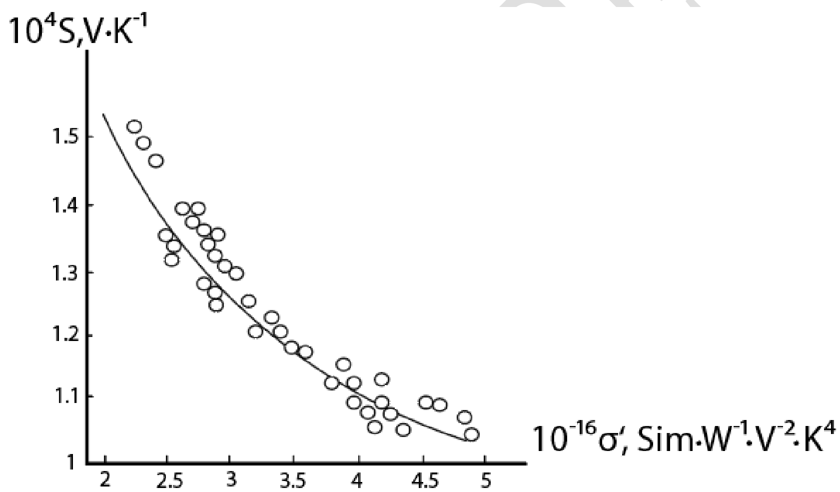

Figure 3. S–σ' dependences. (The points belong to all x values in $Bi_2Sr_{2-x}[Sr(BO_2)_2]_x Co_{1.8}O_y$ and $Bi_2Sr_2Co_{1.8}O_y$+ xGr.)

In addition to the fact that electronic quality factor B_E scales thermoelectric parameters (electrical conductivity, power factor), it is also should be noted that for an ideal material B_E does not depend on temperature. A deviation from this indicates the presence of additional effects.
To determine B_E, we first calculated the values of B_S using the formula [8]:

$$B_S = \frac{\left(\frac{qS}{k_B}\right)^2 e^{2-\frac{qS}{k_B}}}{1+e^{-5\left(\frac{qS}{k_B}-1\right)}} + \frac{\frac{\pi^2 qS}{3k_B}}{1+e^{5\left(\frac{qS}{k_B}-1\right)}} . \quad (9)$$

The temperature dependences of parameters obtained by the equation (9) and $B_E = \sigma S^2/B_S$ are shown in Fig. 4: the values of B_S change slightly for both types of samples; values of B_E are practically constant at first (a sign of ideal case), and then increase. An increase of B_E with temperature indicates the presence of such effects as additional scattering and band convergence [8].

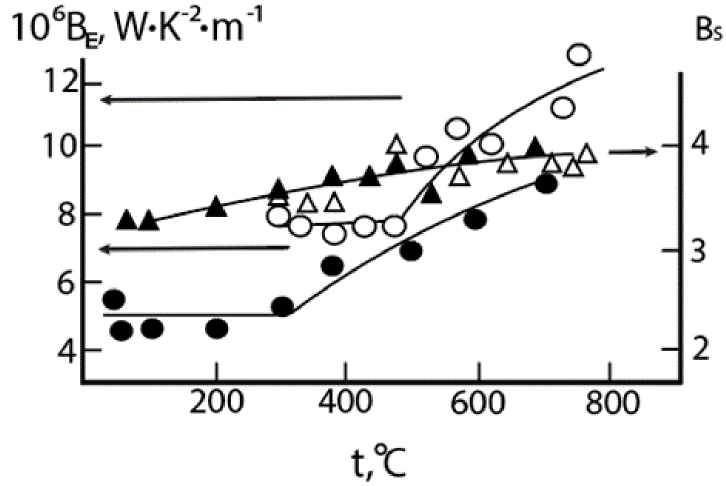

Figure 4. Typical temperature dependences of B_E and B_S: o, Δ - $Bi_2Sr_{1.925}[Sr(BO_2)_2]_{0.075}Co_{1.8}O_y$; ●, ▲ - $Bi_2Sr_2Co_{1.8}O_y$+ 0.35Gr.

3. CONCLUSION

Thus, it can be stated that the dependences of the Seebeck coefficient on the electrical conductivity in the $Bi_2Sr_2Co_{1.8}O_y$ thermoelectric both with the addition of graphene and with the dopant of strontium borate are rectilinear for individual samples. This allows a simple way (without using formula (1)) to calculate the S - σ dependence. The dependences of the Seebeck coefficient on the universal electrical conductivity exhibit a power-law character and practically do not depend on the dopant and additive concentrations (i.e. B_E scales electrical conductivity). Their combination can be described by a single empirical expression $S \cong 6.79 \cdot 10^4 (\sigma')^{-0.526} - 1.5 \cdot 10^{-5}$.

Values of B_E are practically constant at first (up to 300°C for $Bi_2Sr_{1.925}[Sr(BO_2)_2]_{0.075}Co_{1.8}O_y$ and 500°C for $Bi_2Sr_2Co_{1.8}O_y$+ 0.35Gr), a sign of ideal case, and then increase. An increase of B_E with temperature indicates the presence of additional effects.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

REFERENCES

1. Rubesova K. et al. Effect of a Powder Compaction Process on the Thermoelectric Properties of Bi2Sr2Co1.8O Ceramics. Europ. Ceramic Soc. 2015; 35: 525-531.
2. Fan M. et al. Enhanced Thermoelectric Properties of Bi2Sr2Co2Oy by Alkali Metal Element Doping and SiC Dispersion. Ceramics Intern. 2019; 45: 17723-17728.
3. Kuzanyan A. et al. Effect of Sr(BO2)2 Dopant on the Power Factor of Bi2Sr2Co1.8Oy Thermoelectric. Contemporary Physics. 2021; 56: 146-249.
4. Margiani N. et al. Impact of Graphene Addition on the Microstructure and Thermoelectric Properties of Bi2Sr2Co1.8Oy Ceramics. Bull. Georgian Acad. Sci. 2022; 16: 17-24.
5. Snyder G. and Toberer E. Complex Thermoelectric Materials. Nature Materials. 2008; 7: 105-114.
6. Zhao L. et al. Improvement of Thermoelectric Properties and their Correlations with Electron Effective Mass in Cu1.98S x Se1−x. Sci. Reports. 2017; 7: 40436(1-11).
7. Li M. et al. Optimizing Electronic Quality Factor toward High Performance Ge1-x-yTaxSbyTe Thermoelectrics: The Role of Transition Metal Doping. Adv. Materials. 2021; 33: 2102575 (1-8).
8. Zhang X et al. Electronic Quality Factor for Thermoelectrics. Sci. Advances. 2020; 6: eabc0726 (1-5).
9. Zhao L. et al. (2017) Improvement of thermoelectric properties and their correlations with electron effective mass in Cu1.98SxSe1−x. Scientific Reports. 2017; 7: 40436(1-11).
10. Cooley J.A. al. High Seebeck Coefficient and Unusually Low Thermal Conductivity Near Ambient Temperatures in Layered Compound Yb2−xEuxCdSb2 High Seebeck Coefficient and Unusually Low Thermal Conductivity Near Ambient Temperatures in Layered Compound Yb2−xEuxCdSb2. Chem. Mater. 2018; 30: 484-493.
11. Jeong H. et al. High Seebeck coefficient and low thermal conductivity in Bi and In co-doped GeTe thermoelectric material. Materials Res. and Technology. 2021; 15: 6312-6318.