Journal of Materials Science Research and Reviews

Volume 6, Issue 4, Page 670-675, 2023; Article no.JMSRR.104810

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

Irakli Nakhutsrishvili [a*], Giorgi Kakhniashvili [a], Iamze Kvartskhava [a] and Akaki Gigineishvili [b]

[a] *Institute of Cybernetics of Georgian Technical University, Tbilisi, Georgia.*
[b] *Department of Engineering Physics, Georgian Technical University, Tbilisi, Georgia.*

Authors' contributions

This work was carried out in collaboration among all authors. All authors read and approved the final manuscript.

Article Information

Open Peer Review History:
This journal follows the Advanced Open Peer Review policy. Identity of the Reviewers, Editor(s) and additional Reviewers, peer review comments, different versions of the manuscript, comments of the editors, etc are available here: https://www.sdiarticle5.com/review-history/104810

Short Communication

Received: 16/06/2023
Accepted: 22/08/2023
Published: 01/09/2023

ABSTRACT

The Seebeck effect has found its application in many areas of human activity. This effect is applicable in the thermoelectric generators for converting waste heat into electrical energy. $Bi_2Sr_2Co_{1.8}O_y$ ceramics is a promising thermoelectric material. Incorporation of suitable dopants into the $Bi_2Sr_2Co_{1.8}O_y$ host matrix significantly increases the thermoelectric performance of this system. This paper considers the dependence of the Seebeck coefficient on the specific and universal electrical conductivities of $Bi_2Sr_2Co_{1.8}O_y$ 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

**Corresponding author: Email: iraklinakhutsrishvili52@gmail.com;*

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

Because of their ability to directly convert waste heat into electrical power, thermoelectric materials have attracted considerable interest as a source of environmentally friendly energy to address the energy crisis and ecological issues. Layered cobaltites are promising materials for high-temperature thermoelectric generators [1,2]. Doping method is widely used in order to enhance their functional efficiency, in particular, increase the power factor PF=σS^2, where σ is the electrical conductivity, S is the Seebeck coefficient [3-5]. Based on previously reported data, the dependences of the Seebeck coefficient on the specific and universal electrical conductivities in $Sr(BO_2)_2$ [6] and graphene-doped [7] $Bi_2Sr_2Co_{1.8}O_y$ thermoelectrics were investigated in this paper.

2. METHODOLOGY

In the theory of semiconductors, in the relevant sections, the dependence of the Seebeck coefficient on the characteristics of charge carriers is defined as [8-10]:

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

where n is the concentration of charge carriers, m* is the effective mass, q is the elementary charge, T is absolute temperature, k_B and h are the Boltzmann and Planck constants, respectively. Taking into account the expression for electrical conductivity σ=nqμ (μ - mobility) and the values of universal constants, formula (1) will take the form:

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

The concept of universal electrical conductivity is also introduced:

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

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 [11]. Using Eqs.(2) and (3):

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

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.

3. RESULTS AND DISCUSSION

It should be noted that the comparative narrowness of the range of the Seebeck coefficient change ((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 doped samples the dependences σS^2–S are rectilinear (Fig. 1):

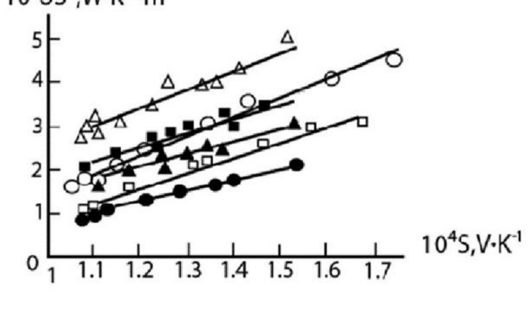

Fig. 1. Dependences of the power factor on the Seebeck coefficient: $Bi_2Sr_{2-x}[Sr(BO_2)_2]_xCo_{1.8}O_y$ – (o) x=0.075, (△) x=0.1, (□) x=0.15; $Bi_2Sr_2Co_{1.8}O_y$+ xGr – (●) x=0.35, (▲) x=0.7, (■) x=1.15

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

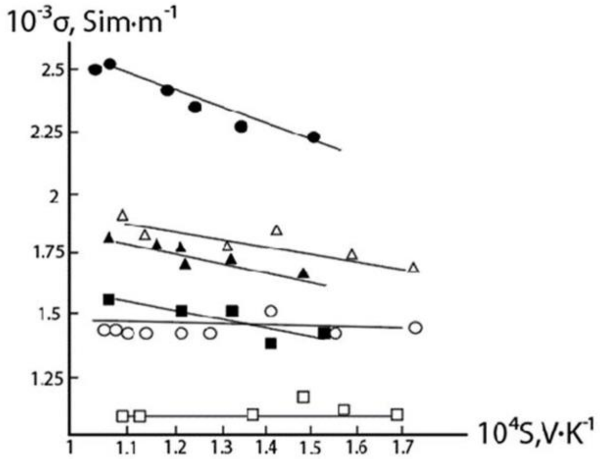

Fig. 2. Implicit dependences $S-\sigma$: $Bi_2Sr_{2-x}[Sr(BO_2)_2]_xCo_{1.8}O_y$ – (o) x=0.075, (△) x=0.1, (□) x=0.15; $Bi_2Sr_2Co_{1.8}O_y$+ xGr – (●) x=0.35, (▲) x=0.7, (■) x=1.15

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

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).

Eq.(5) can be rewritten as:

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

Fig.2 shows the dependence S– σ in the 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. For comparison, we plotted these dependences for larger ranges of S change (up to (2.5-5) $\cdot 10^{-4} V \cdot K^{-1}$) for other thermoelectrics [12,13]. A deviation from straightness was observed, which follows from the above formulas.

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 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 (according to data of [6] and [7]). Since σS^2 depends on S more than on σ, this results is an increase of the power factor.

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 the dopants (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 σ' $- B_S/S^2$, constructed according to formula (7), will have the same form for any thermoelectric – the form of a straight line with a slope of ≅1.347∗10^8 SimW^{-1}K^2.)

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 B_E does not depend on temperature for an ideal material. 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 [11]:

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

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 [11].

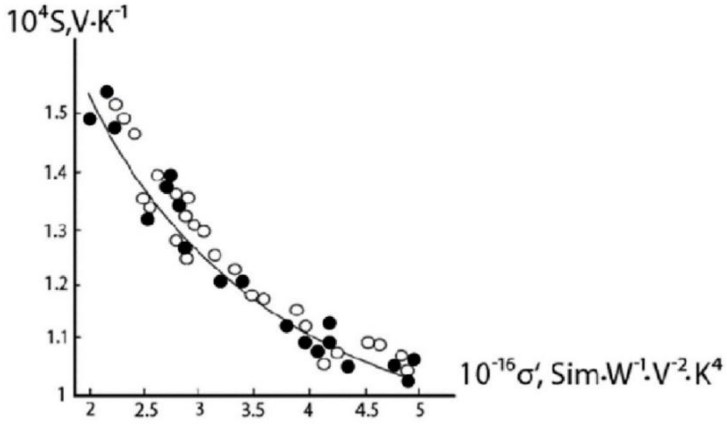

Fig. 3. S–σ' dependences: (o) – $Bi_2Sr_{2-x}[Sr(BO_2)_2]_xCo_{1.8}O_y$, (●) – $Bi_2Sr_2Co_{1.8}O_y$+ xGr

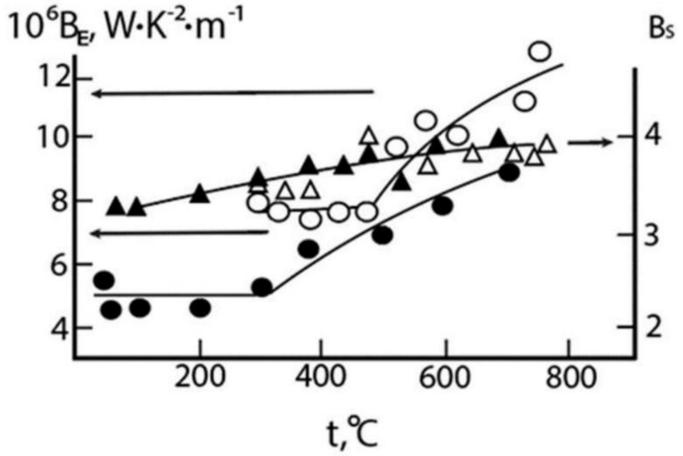

Fig. 4. Typical temperature dependences of B_E and B_S: o, △ - $Bi_2Sr_{1.925}[Sr(BO_2)_2]_{0.075}Co_{1.8}O_y$; ●, ▲ - $Bi_2Sr_2Co_{1.8}O_y$+ 0.35Gr

4. CONCLUSION

Thus, it can be stated that the dependences of the Seebeck coefficient on the electrical conductivity in the $\mathrm{Bi_2Sr_2Co_{1.8}O_y}$ thermoelectric ceramics doped with the strontium borate and graphene are rectilinear for individual samples. This provides a simple way to calculate the S - σ dependence without using formula (1). The dependences of the Seebeck coefficient on the universal electrical conductivity exhibit a power-law character, practically do not depend on the concentration of dopants (i.e. B_E scales electrical conductivity), and can be described by a single empirical expression $S \cong 6.79 \cdot 10^4 (\sigma')^{-0.526} - 1.5 \cdot 10^{-5}$. For all the samples, the values of the electronic quality factor were calculated and their temperature dependences were plotted. Values of B_E are practically constant up to 300 ºC for $\mathrm{Bi_2Sr_{1.925}[Sr(BO_2)_2]_{0.075}Co_{1.8}O_y}$ and 500 ºC for $\mathrm{Bi_2Sr_2Co_{1.8}O_y}$ + 0.35 wt % Gr, a sign of ideal case, and then increase. An increase of B_E with temperature indicates the presence of additional effects (additional scattering and band convergence).

ACKNOWLEDGEMENT

This work was supported by Shota Rustaveli National Science Foundation of Georgia (SRNSFG) [PHDF-22-442/Influence of borax doping on the thermoelectric performance of layered cobaltites].

COMPETING INTERESTS

Authors have declared that no competing interests exist.

REFERENCES

1. Rubesova K, Hlásek T, Jakes V, et al. Effect of a powder compaction process on the thermoelectric properties of $Bi_2Sr_2Co_{1.8}O$ ceramics. Europ. Ceramic Soc. 2015;35: 525-531.
2. Fan M, Zhang Y, Hu Q, et al. Enhanced thermoelectric properties of $Bi_2Sr_2Co_2Oy$ by alkali metal element doping and SiC dispersion. Ceramics Intern. 2019;45: 17723-17728.
3. Ozcelik B, Gürsul M, Çetin G, et al. Detail investigation of thermoelectric performance and magnetic properties of Cs-doped $Bi_2Sr_2Co_2Oy$ ceramic materials. Appl. Sci. 2021;3:art.# 114.
4. Hira U, Pryds N, Sher F. Thermoelectric properties of dual doped $Bi_2Sr_2Co_2O_y$ $Bi_2Sr_2Co_2O_y$ Based Ceramics. Electronic Materials. 2019;48:4618–4626.
5. Mumladze G, Kvartskhava I, Klyndyuk A, Zhghamadze VV, Margiani NG, A.S. Kuzanyan AS. Effect of Pb(BO2)2 doping on power factor of Bi2Sr2Co1.8Oy thermoelectric ceramics. Acta Phys. Polonica A. 2022;141:319-322.
6. Kuzanyan A, Margiani N, Zhghamadze V, et al. Effect of $Sr(BO_2)2$ dopant on the power factor of $Bi_2Sr_2Co1_{.8}O_y$ thermoelectric. Contemporary Physics. 2021;56:146-249.
7. Margiani N, Zhghamadze V, Mumladze G, et al. Impact of graphene addition on the microstructure and thermoelectric properties of $Bi_2Sr_2Co_{1.8}O_y$ ceramics. Bull. Georgian Acad. Sci. 2022;16: 17-24.
8. Snyder G, Toberer E. Complex thermoelectric materials. Nature Materials. 2008;7:105-114.
9. Zhao L, Fei FY, Wang J, et al. Improvement of thermoelectric properties and their correlations with electron effective mass in $Cu_{1.98}S_xSe_{1-x}$. Sci. Reports. 2017;7:40436(1-11).
10. Li M, Sun Q, Xu Ch.-D, et al. Optimizing electronic quality factor toward high performance $Ge_{1-x-y}Ta_xSb_yTe$ thermoelectrics: The role of transition metal doping. Adv. Materials. 2021;33: 2102575 (1-8).
11. Zhang X, Bu Z, Shi X, et al. Electronic quality factor for thermoelectrics. Sci. Advances. 2020;6: eabc0726 (1-5).
12. Cooley JA. Promkhan P, Gangopadhyay Sh, et al. High Seebeck coefficient and unusually low thermal conductivity near ambient temperatures in layered Ccompound $Yb_{2-x}Eu_xCdSb_2$. Chem. Mater. 2018;30:484-493.
13. Jeong H, Kihoi SK, Kim 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.

APPENDIX

$Bi_2Sr_{2-x}[Sr(BO_2)_2]_xCo_{1.8}O_y$ (x = 0.075, 0.1 and 0.15) and $Bi_2Sr_2Co_{1.8}O_y$ + x wt. % Gr (x=0.35, 0.7 and 1.15) ceramic samples were prepared by standard solid-state reaction method from reagent-grade powders of bismuth oxide (Bi_2O_3), strontium carbonate ($SrCO_3$), cobalt oxide (Co_3O_4) and graphene nanopowder (purity: 99.2%, average flake thickness: 12 nm (30–50 monolayers), average particle (lateral) size: 4.5 µm).

(a) $Bi_2Sr_{2-x}[Sr(BO_2)_2]_xCo_{1.8}O_y$: mixtures of initial powders were mixed and subjected to heat treatment at 750–830°C for 30 hours with intermediate grinding in an agate mortar at 830°C for 25 hours. Then the powders were pressed into pellets with a diameter of 15 mm at a hydrostatic pressure of 200 MPa. Finally, the pellets were annealed at 830°C. Cooling to room temperature was carried out for 15 h in the furnace.

(b) $Bi_2Sr_2Co_{1.8}O_y$ + xGr: The mixtures of powders were homogenized in a planetary mill (Fritsch Pulverisette 7 Premium line) for 1 h at a rotating speed of 120 rpm. After homogenization, the powders were calcined at 770–815°C for 18 hours with intermediate grindings in an agate mortar, then pressed into pellets at a hydrostatic pressure of 220 MPa. Finally, the pellets were sintered at 1103–1108 K in air for 20 h, then cooled to room temperature in the furnace.

The phase purity and microstructure of the prepared materials were examined using X-ray diffraction (Dron–3M, CuKα–radiation) and scanning electron microscopy (VEGA TS5130MM) techniques. The resistivity of the samples as a function of temperature ρ(T) was measured by the standard four-probe method. The temperature dependence of the Seebeck coefficient was determined with a homemade setup using a KEITHLEY DMM6500 multimeter.

Peer-review history:
The peer review history for this paper can be accessed here:
https://www.sdiarticle5.com/review-history/104810