Determination of the characteristics of thermoelectrics with high and ultra-high values of the Seebeck coefficient

ABSTRACT

The obtaining and study of materials with high values of the Seebeck coefficient is one of the main factors for the efficient operation of thermoelectric devices. Values of the Seebeck coefficient exceeding $2 \cdot 10^{-4}$V/K are considered to be high values.

This article analyzes works in which high and ultra-high values of the Seebeck coefficient were obtained. The new formula is used to calculate resistivity, carrier concentration or Seebeck coefficient in cases where one of these parameters is not measured or calculated.

The scaled power factor (SPF) of a number of thermoelectric materials is analyzed. The graph of its dependence on the Seebeck coefficient agrees well and complements the graph known from the literature for a large number (more than 3500) of samples towards higher values of the Seebeck coefficient.

Based on the values of SPF and resistivity (or conductivity), the electronic quality factor of some materials is calculated. Its temperature dependence provides information about the mechanism of charge carrier scattering.

The universal electrical conductivity is calculated. Its temperature dependence and the dependence of the Seebeck coefficient on it confirm that the electronic figure of merit scales the thermoelectric parameters of materials.

Keywords: Thermoelectric; high and ultra-high values of the Seebeck coefficient.

I. INTRODUCTION

Devices based on the Seebeck effect are widely used in industrial and household generators, navigation (including space) systems, solar energy converters, etc. The Seebeck coefficient (S) is a measure of the magnitude of the induced voltage. Obtaining and researching of materials with its high values is one of the main factors for the effective operation of the above-mentioned devices. An important factor of thermoelectrics is also the scaled power factor, which is given by the expression [1]:

$$B_S = S_r\left[\frac{S_r e^{(2-S_r)}}{1+e^{-5(S_r-1)}} + \frac{\pi^2}{3[1+e^{5(S_r-1)}]}\right], \quad (1)$$

where $S_r=(q_e/k_B)S\cong 1.1605\cdot 10^4 S$ is the reduced Seebeck coefficient, and q_e , k_B are elementary charge and Boltzmann's constant, respectively.

The paper [1] shows also the dependence of the scaled power factor on the Seebeck coefficient for a large number (more than 3500) of samples at $(0<S\leq 6)\cdot 10^{-4}$V/K. Values of S greater than $2\cdot 10^{-4}$V/K can already be considered high values of the Seebeck coefficient. In a number of works, ultra-high values of this coefficient ($>1\cdot 10^{-3}$V/K) are given. Here we will consider works in which high and ultra-high values of the Seebeck coefficient were obtained. In such cases, instead of equation (1) you can use: $B_S\cong S_r^2 e^{(2-S_r)}$, the accuracy of which increases with increasing Seebeck coefficient, and instead of equation (2) (see below) you can use: $S_r^2 e^{(2-S_r)}\cong 1.087\cdot 10^{-9}(\rho n)^{2/3}S$.

Using the Seebeck coefficient, the effective mass of charge carriers is calculated, and then the mobility is calculated using the formulas given in [2-5].

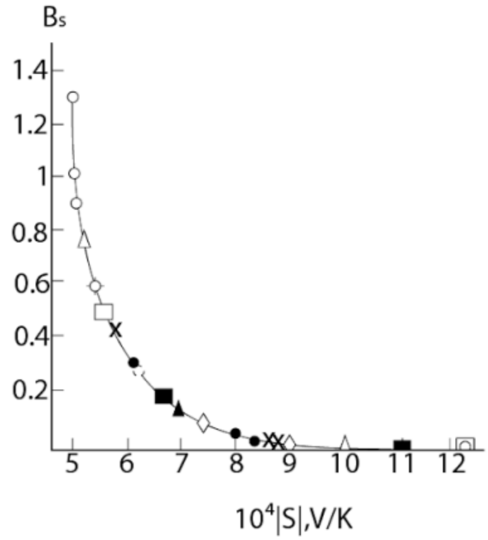
3. METHODOLOGY

As already mentioned in the introduction, in this article we consider works in which high and ultra-high values of the Seebeck coefficient were obtained. We present data for a certain number of different thermoelectric materials. The relevant methods can be found in the cited references. Below we provide data on the method of preparing our samples a silicon-germanium alloy.

We made SiGe alloys with n-type conductivity. The method of joint grinding of the components and vacuum hot pressing of the obtained ultradisperse powder was used. The alloying element for n-type conduction was phosphorus (0.5 wt.%). The concentration of charge carriers was $3.2\cdot10^{20}$cm^{-3}. It was defined by measuring the Hall constant at room temperature. The grain sizes of the powder were evaluated with an optical microscope “Nicon” and an X-ray diffractometer DRON-3M. Ultradisperse powder consisted mainly of 60–80 nanometer Si and Ge grains. The resulting powder was pressed in a high-temperature vacuum induction pressure chamber at a temperature of 1200-1320°C and a pressure of 480 kg·cm^{-2} for 20-30 minutes. The matrix and punches are made of high strength graphite. From the obtained briquettes, profiled samples were cut out on a diamond-cutting disk device.

3. RESULTS & DISCUSSION

Fig. 1a,b shows the results calculated from the data of the literature [6-18] for such values of the Seebeck coefficient.(*) These data extend well the graph presented in [1] towards higher values of S. It should be noted that some of the works cited above do not mention the values of the Seebeck coefficient, because the emphasis is on the study of other parameters. However, of the proposed equation [28]: $\frac{e^{(11605S-2)}}{S[1+e^{-5(11605S-1)}]}+\frac{3527.5}{1+e^{5(11605S-1)}} \cong 1.087\cdot10^{-9}(\rho n)^{2/3}$, S can also be calculated using the values of ρ (specific resistivity) and n (charge carrier concentration). This equation can be used for the complete analysis of the papers in which one of the values of S, ρ or n is not given.(**)


Bs
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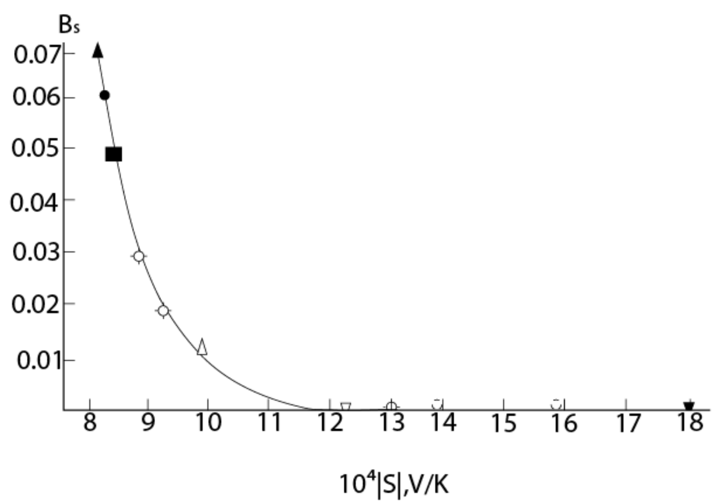
$10^4|S|$,V/K

(a)


Bs
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8 9 10 11 12 13 14 15 16 17 18
$10^4|S|$,V/K

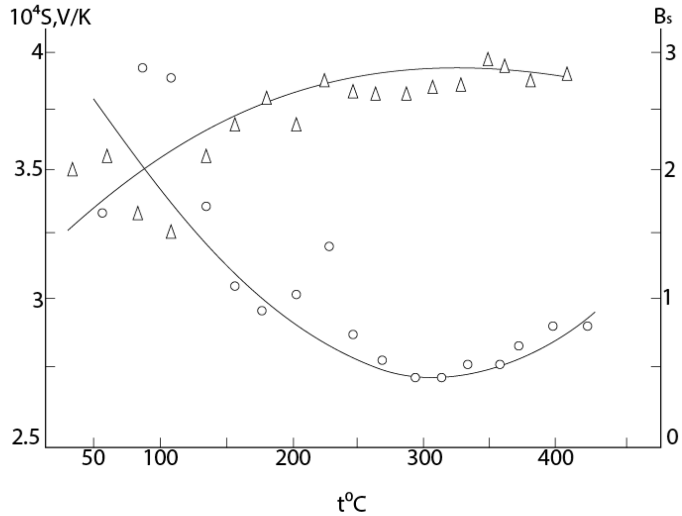
(b)

Fig. 1. (a) Dependence of the scaled power factor on the Seebeck coefficient, calculated according to the data for following thermoelectrics: (o)$Cu_3Sb_{1-x}Bi_xSe_4$ [6], (Δ)$SrTiO_3$ [7],(□) $CH_3NH_3PbI_3$ [8], ◌ SiGe [9], (●) $SnSe_{1-x}Te_x$ [10], (■) GCuO[11], (⌖) $PbSb_xTe_{1-x}$ [12], (⧇)$PtSe_2$ [13], (▲) CuGeTe [14], (▼) Si [15]; (x) $La_{0.95}Sr_{0.05}CoO_3$ [16]; solid line is a fragment of the averaged curve given in [1]; (b) the same - in another scale on the ordinate axis.

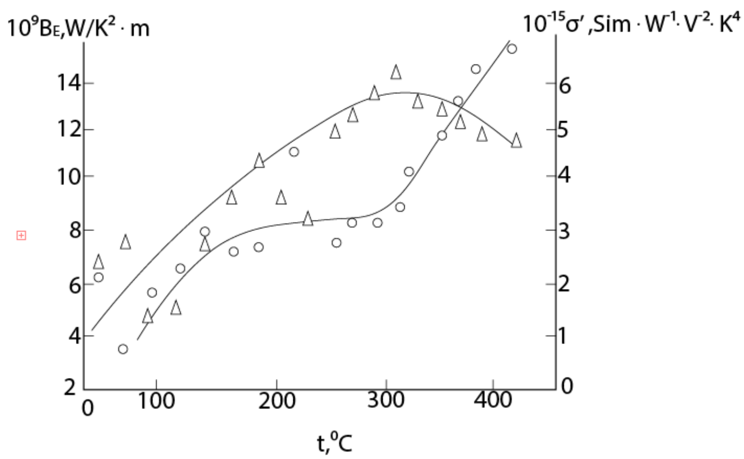
Using experimentally measured values of the Seebeck coefficient or values calculated by equation (2), as well as the value of specific resistivity (or specific electrical conductivity $\sigma=1/\rho$), it is possible to calculate such an important parameter of thermoelectric materials as the electronic quality factor: $B_E=\sigma S^2/B_S$. By means of its temperature dependence, it is possible to obtain information on the mechanism of scattering of charge carriers in the material [1]. After calculating the electronic quality factor, it is possible to calculate the universal electrical conductivity: $\sigma'=(q_e/k_B)^2\sigma/B_E \cong 1.347\cdot10^8\sigma/B_E$).

In order to substantiate the reliability of the above formulas at high values of the Seebeck coefficient, let us consider some data from the literature.

In work [32] N-type $Si_{0.96}Ge_{0.04}$ was irradiated with ^{60}Co gamma photons and the electrical resistance, concentration, and mobility of charge carriers were measured. Seebeck coefficient and other thermoelectric characteristics were not studied in this work. These parameters were calculated in [28] for the temperature range (250-430)^oC. Data up to 25^oC has been added here (Fig. 2).



(a)

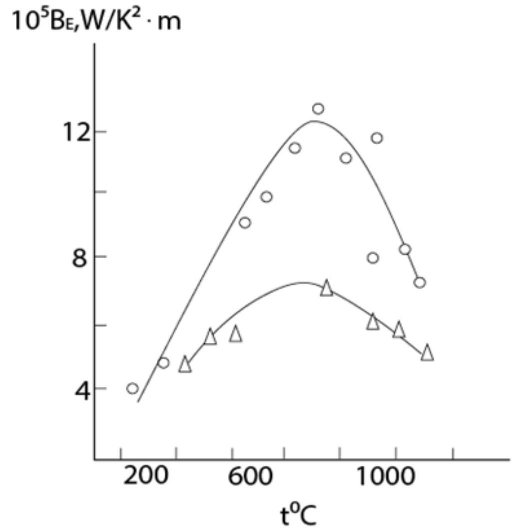


(b)

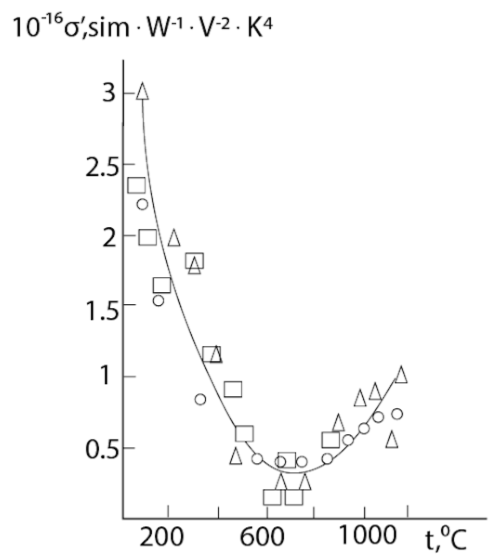
Fig.2. (a) Dependences (o) S – t and (Δ) B_S – t for $Si_{0.96}Ge_{0.04}$ irradiated with gamma photons. (t – isochronal annealing temperature).

(b) B_E – t(o) and σ'- t dependences (Δ).

The dependences B_E - t and σ'-t differ significantly from the data for Si_xGe_{1-x} samples without irradiation (Fig. 3) and from them it is difficult to conclude about the mechanism of charge carrier scattering (see footnote [**]) .



(a)



(b)

Fig. 3. (a) B_E - t dependences for $Si_{0.7}Ge_{0.3}$: (o) N-type, (Δ) P-type [28,30].

(b) σ'- t dependences for N-type: (o) $Si_{0.7}Ge_{0.3}$ and (∆) $Si_{0.83}Ge_{0.17}$ and (□) $Cu_{1.98}S$[29,30,33].

In work [32], all parameters of ceramic $Na_{0.55}Co_{0.9}W_{0.1}O_2$ were measured or calculated, except for the effective mass (m*) and mobility (μ) of charge carriers. The ratio m^*/m_0 (m_0- rest mass) can be calculated using the formula:

$$\frac{m^*}{m_0} \cong 1.059\cdot10^{-15}\left(\frac{n^{2/3}}{T}\right)\left\{\frac{3\left[e^{(S_r-2)}-0.17\right]^{2/3}}{1+e^{-5(S_r-S_r^{-1})}}+\frac{S_r}{1+e^{5(S_r-S_r^{-1})}}\right\} \cong \frac{6.608\cdot10^{-15}}{T}\left[ne^{(S_r-2)}\right]^{2/3}, \quad (3)$$

where T is absolute temperature. The value of m^*/m_0 calculated using Eq.(3) at 1167K turned out to be $3.33\cdot10^{-3}$. This value could be considered very (unacceptable) low, but then, using the formula $\mu=(m^*/m_0)^{-3/2}\mu_W$ (μ_W - weighted mobility), a very real value of mobility was obtained: $\mu \cong 3.25\cdot10^{-2} m^2/V\cdot s$.

In work [33], all parameters of $Cu_{1.98}S_xSe_{1-x}$ were determined, except for the electronic quality factor and universal electrical conductivity. From the temperature dependence of B_E we calculated, it is difficult to draw a definite conclusion about the mechanism of charge carrier scattering. And shown in Fig. 3(b) the temperature dependence of the universal electrical conductivity, together with the data for Si_xGe_{1-x}, shows that all experimental points form a regular set, despite the differences in the samples. This confirms that the electronic quality factor B_E scales the electrical conductivity of materials. (***)

Footnotes:

(*) Points corresponding to higher values of S according to some of the works cited above are not shown based on the scale of the figure. Much higher values were obtained for polymers PEDOT:PSS [18], O+NaOH [19], PSSH+PANI-CNT [20], NFC-PSSNa [21], Nafion, S-PEEK[22], PEDOT-Tos+CNT[23], $(poly(3\text{-}hexylthiophene))_xB_{1-x}$ [24], as well as for Si(ICs) [25], $CsGeX_3$(x=F, Cl, Br) [26] and others.

(**) The shape of the curves in Fig. 3(a) indicates that in Si_xGe_{1-x},with increasing temperature, additional scattering is accompanied by convergence of the bands, and then by bipolar effects.

(***) B_E scales the electrical conductivity also in the σ'-S and σ'-σ coordinates [28-30].

4. CONCLUSION

This Article analyzes works in which high and ultra-high values of the Seebeck coefficient were obtained. A new formula is used to calculate resistivity, carrier concentration or Seebeck coefficient in cases where one of these parameters is not measured or calculated.The scaled power factor, universal electrical conductivity and electronic quality factor of a number of thermoelectric materials has been analyzed. Temperature dependence of electronic quality factor indicates that in alloy Si_xGe_{1-x} with increasing temperature additional scattering is accompanied by band convergence, and then by bipolar effects.Temperature dependence of universal electrical conductivity confirm that the electronic quality factor scales thermoelectric parameters.

REFERENCES

1. Zhang X, Bu Z, Shi X et al. Electronic quality factor for thermoelectrics. Sci. Adv. 2020; 6: eabc0726.

2. Zuo G, Liu X, Fahlman M, Kemerink K. High Seebeck coefficient in mixtures of conjugated polymers. Adv. Funct. Materials. 2018; 28: 1703280.

3. Sreeram PR, Nair NM, Dayal G et al. Ultra-high Seebeck coefficient of nanostructured Sb-substituted PbTe and fabrication of a thermoelectric generator module. Bull. Materials Sci. 2021; 44: 9.

4. Nedunchezhian A, Rajkumar R, Devi NY. Effect of Te substitution on the enhancement of thermoelectric. Bull. Materials Sci. 2021; 44: 1.

5. Duraisamy S, Nedunchezhian A., Rajkumar R et al. Effect of Te substitution on the enhancement of thermoelectric power factor of nanostructured $SnSe_{1-x}Te_x$. PhysCemChemPhys. 2019; 28: 1.

6. Liu Y., Ortega S, Cadavid D. et al. Solution-synthesis and processing of Sn- and Bi-doped Cu_3SbSe_4 nanocrystals, nanomaterials and ring-shaped thermoelectric generators. Materials Chem. A. 2017; 5: 2592.

7. Jalana B, Stemmerb S. Large Seebeck coefficients and thermoelectric power factor of La-doped $SrTiO_3$ thin films. Appl. Phys. Lett. 2010; 97: 0421062010.

8. Pan Z, Zhu Z, Wilcox J et al. Tackling challenges in Seebeck coefficient measurement of ultra-high resistance samples with an AC technique. Adv. Electronic Materials. 2020; 6: 1901340.

9. Xu Q, Zhou J, Liu TH, Chen G. First-principles study of all thermoelectric properties of Si–Ge alloys showing large phonon drag from 150 to 1100 K. Phys.Rev. Appl. 2021; 16: 064052.

10. Duraisamy S, Nedunchezhian A, Rajkumar R et al. Effect of Te substitution on the enhancement of thermoelectric power factor of nanostructured $SnSe_{1-x}Te_x$. PhysChemChemPhys. 2019; 28: 15725.

11. Andrei V, Bethke K, Rademan K. Adjusting the thermoelectric properties of copper(i) oxide–graphite–polymer pastes and the applications of such flexible composites. PhysChemChemPhys. 2016; 18: 10700.

12. Sreeram PR, Nair NM, Gopalakrishnan D et al. Ultra-high Seebeck coefficient of nanostructured Sb-substituted PbTe and fabrication of a thermoelectric generator module. Bull. Mater. Sci. 2021; 44: 9.

13. Moon H, Bang J, Hong S et al. Strong thermopower enhancement and tunable power factor via semimetal to semiconductor transition in a transition metal dichalcogenide. ACS Nano. 2019; 13: 13317.

14. Onio A, Goncalves AP, Lopez E et al. Conducting glasses as new potential thermoelectric materials: The Cu-Ge-Te case. Materials Chem. 2010; 20: 1516.

15. Hase M., Tanisawa D, Kohashi K et al. Determination of Seebeck coefficient originating from phonon-drag effect using Si single crystals at different carrier densities. Sci. Rep. 2023; 13: 13463.

16. Androulakis J, Migiakis P, Giapintzakis J. $La_{0.95}Sr_{0.05}CoO_3$: An efficient room-temperature thermoelectric oxide. Appl. Phys. Lett. 2004; 84: 1099.

17. Serrano-Sanchez F, Gharsallah M, Nemes NM et al. Record Seebeck coefficient and extremely low thermal conductivity in nanostructured SnSe. Appl. Phys. Lett. 2015; 106: 083902.

18. Chang WB, Fang H, Liu J et al. Electrochemical effects in thermoelectric polymers. ACS Macro Lett. 2016; 5: 455.

19. Zhao D, Wang H, Khan ZUet al. Ionic thermoelectric supercapacitors. Energy Environ. Sci. 2016; 9: 1450.

20. Kim SL, Lin HT, Yu C. Thermally chargeable solid-state supercapacitor. Adv. Energy Mater. 2016; 6: 1.

21. Jiao F, Naderi A, Zhao D et al. Ionic thermoelectric paper. Mater. Chem. 2017; 5: 1688.

22. SKim SL, JHsu J-H, Yu C. Thermoelectric effects in solid state polyelectrolytes. Org. Electron. 2018; 54: 231.

23. Choi K, Kim SL, Yi S et al. Promoting dual electronic and ionic transport in PEDOT by embedding carbon nanotubes for large thermoelectric responses. ACS Appl. Mater. Interfaces. 2018; 10: 23891.

24. Zuo G, Liu X, Fahlman M, M.Kemerink M. High Seebeck coefficient in mixtures of conjugated polymers. Adv. Funct. Materials. 2018; 28: 1703280.

25. Van Herwaarden AW. The seebeck effect in silicon ICs. Sens. Actuators. 1984; 6: 245.

26. Bouhmaidi S, Marjaoui A, Talbi A et al. A DFT study of electronic, optical and thermoelectric properties of Ge-halide perovskites $CsGeX_3$ (X=F, Cl and Br). Computat. Condens. Matter. 2022; 31: e00663.

27. Tkhinvaleli R, Loria L, Adamia Z, I.Nakhutsrishvili. Determination of the Seebeck coefficient and other thermoelectric parameters using specific resistivity and concentration of charge carriers of N-$Si_{0.96}Ge_{0.04}$ alloy irradiated by 60Co γ-photons. Phys. Sci. IJ. 2024; 28: 16.

28. Bokuchava G, Barbakadze K, Nakhutsrishvili I. On the thermoelectric alloy n-Si_xGe_{1-x}. Material Sci. & Engin. 2023; 7: 54.

29. Barbakadze K, Kakhniashvili G, Nakhutsrishvil I. Determination of electronic quality factor, universal electrical conductivity, effective mass and mobility of charge carriers of alloy n-Si_xGe_{1-x}. Materials Sci. Res. and Rev. 2023; 6: 730.

30. Bokuchava G, Barbakhadze K, Nakhutsrishvili I. Thermoelectric parameters of alloy p-$Si_{0.7}Ge_{0.3}$. Bull. Georg. Acad. Sci. 2023; 17: 33.

31. Kurashvili I, Kimeridze T, Chubinidze G et al. Electrophysical properties of monocrystalline n-Si+0.4at%Ge:P alloy irradiated by ^{60}Co gamma photons. Georg. Scient. 2022; 4: 74.

32. Krasutskaya NS, Klyndyuk A. Thermoelectric ceramics based on the layered sodium cobaltite. Proc. X Int. Conf. Materials and Structures of Modern Electronics. Minsk, Belarus. 2022: 122.

33. Zhao L, Fei FY, Wang G 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.