Kinetic laws of the thermovoltaic effect in semiconductor structures based on samarium sulfide

M A Grevtsev, S A Kazakov, G D Havrov, M M Kazanin, N V Sharenkova, S M Solov’ev and S G Shulman
Laboratory of physics of rare-earth semiconductors, Ioffe Institute, Saint Petersburg 194021, Russia

E-mail: gma114@mail.ioffe.ru

Abstract. The experimental data on the thermovoltaic effect in bulk samples of samarium sulfide (SmS) are considered in this work in accordance with the represented kinetic model. The kinetic laws of the elementary process of samarium ions ionization have been studied, expressions are obtained for both the dynamics of the ionization process and the process statics in the context of the law of mass action in bulk samples of samarium sulfide. Such a description of the thermovoltaic effect made it possible to obtain the current-voltage characteristics of the samples at a constant temperature. All basic parameters were obtained for the thermovoltaic generator being developed: short circuit current and open circuit voltage; the internal resistance of the generator as well as the maximum power dissipation at the found load resistance was determined by calculation.

1. Introduction
A kinetic model for describing the thermovoltaic effect arising at a constant temperature in bulk samples of samarium sulfide (SmS) is proposed in this work. The authors suggested in [1], that the cause of this effect is the thermal casting of electrons into the conduction band of the semiconductor at constant supply of heat. In this case, samarium ions located in the interstitial sites of the crystal lattice participate in the collective electronic transition [2]; their nonequilibrium concentration gradient is produced during high-temperature annealing of the polycrystalline, the technology of which is described in [3].

2. Kinetic model
The elementary process of electron transfer into the conduction band of a semiconductor is described by the kinetic ionization equation of samarium ions:

\[(\text{Sm}^{2+}_v) = (\text{Sm}^{3+}_v) + e^- \] (1)

According to the law of mass action, when the density of electron states in the impurity region of a wide-gap semiconductor is much lower than the density of electron states in the conduction band [4], we can write down the rate of decrease of conduction electrons in time of such a samarium sulfide polycrystalline structure in the form:

\[d[e^-]/dt = k_2[(\text{Sm}^{2+}_v)] - k_1[(\text{Sm}^{3+}_v)][e^-] \] (2)
where \( k_1 \) and \( k_2 \) are the rate constants of the forward and reverse reactions, respectively, and the square brackets \([\ ]\) indicate the current concentration of electrons (the main charge carriers in samarium sulfide) and the current concentrations of twice and thrice ionized samarium atoms.

The following assumptions are made:

\( a) \quad [e^+] = [(Sm^{3+})]_i, \) since the molar concentrations in the equation of the ionization reaction of samarium (\(^{(*)}\) are equal;

\( b) \quad [(Sm^{2+})]_i = N_d - [e^+], \) where \([(Sm^{2+})]_i \) – concentration of the initial twice-ionized samarium atoms, \( N_d \) and \([e^+]\) are the current concentration of electrons in the SmS conduction band and the concentration of interstitial samarium ions (obtained by annealing the polycrystalline), respectively, \([(Sm^{3+})]_i \) - concentration of interstitial thrice-ionized samarium atoms.

Using the above assumptions, the following process equation can be obtained for the rate of change of the dimensionless quantity of the electrical conductivity of the sample at a constant temperature of samarium sulfide:

\[
\frac{dx}{dt} = k_2 - k_2x - k_1\frac{\sigma x^2}{q u}
\]

where \( x = \sigma/\sigma_0 \) - is the dimensionless electrical conductivity of samarium sulfide, \( q \) and \( u \) are the charge and mobility of charge carriers (electrons) in samarium sulfide, respectively.

We obtained an expression for the process statics after integrating the relation (3):

\[
x_e = 2/(1+(1+4k_1\sigma_0/k_2 q u)^{1/2})
\]

which is similar to the views of Bube [5] on photoconductivity in semiconductor structures of solids for “dark” experimental conditions.

Consideration of the observed experimental data on the thermovoltaic effect in bulk samples of samarium sulfide within the framework of the kinetic model allowed us to describe the current-voltage characteristics of the samples. Thus the equation (3) is valid for the dynamics of the process at any time, but the expression (4) is obtained for the statics of the process. The expression (4) describes the stationary values of the dimensionless conductivity of the sample at a constant process temperature and is consistent with the main conclusions of [4], which allows to unambiguously describe the current-voltage characteristics of the developed samples of thermovoltaic converters of thermal energy into electrical energy.

3. Results of measurements

The internal resistance as well as the maximum power dissipation of a generator was determined by calculation at the found load resistance. The studied thermovoltaic element (TE) was made according to [3] and consisted of a 10 \( \times \) 5 \( \times \) 5 mm polycrystalline of semiconductor SmS, which was soldered to a cobalt plate using a metal samarium. The useful signal was taken from the output contacts attached on one side to this plate and, on the other side, to the SmS polycrystalline. During soldering and subsequent annealing of the polycrystalline, samarium diffused into a bulk SmS sample with the formation of a nonequilibrium gradient of excess samarium ions (stabilized presumably in the interstices of the SmS crystal structure), which is necessary for the appearance of a thermovoltaic concentration effect.

The electrical characteristics of the obtained thermovoltaic effect were obtained by measuring the generated voltage of emf and current sample temperature over time. In this case, an electrical voltage was recorded in a semiconductor SmS in the direction of the gradient of the local concentration of excess samarium ions, starting from room temperatures and above. The results of such measurements are presented in figure 1. Connection of various load resistances was carried out in parallel to the measuring circuit at the maximum temperature of the experiment. When the circuit closes to the payload, an electric current appears and the voltage drop of the registered emf is recorded (curve 1, figure 1). Disconnection of the load leads to the regeneration of the initial voltage. We used the
experimentally obtained current-voltage characteristic to calculate the parameters of the thermovoltaic generator.

![Graph](image1)

**Figure 1.** Dependences of the voltage generated by a thermovoltaic element based on samarium sulfide (1) and the current temperature (2) of the process in time.

The “steps” on the decline of curve 1 (figure 1) correspond to the voltage drop of the emf when connecting a payload of various nominal resistance from 1000 to 0.5 Ohm. As is well known [6], the current of the thermoelectric generator is maximum and equal to $I_{sc}$ in the short circuit mode. The typical current-voltage characteristic is a straight line making an angle $\beta$ with the axis of the electric current, and $tg\beta = r_{te}$, where $r_{te}$ is the internal resistance of the thermovoltaic element. Figure 2 shows the obtained in our experiment current-voltage characteristic for a typical thermovoltaic element based on samarium sulfide, which fully corresponds to the current-voltage characteristic of a typical thermoelectric generator. In this case, the short circuit current was $I_{sc}=14.5 mA$.

The dependence of the TE power on the electric current (figure 3) can be estimated using the current-voltage characteristic (figure 2), and the formula: $P=I(U-Ir_{te})$.

![Graph](image2)

**Figure 2.** Current-voltage characteristic of the thermovoltaic element.
The quadratic parabola (figure 3) shows that the operating current at maximum power \( I \approx 0.5 \cdot I_{sc} \). The load resistors were connected at temperature \( T = 453 \text{ K} \).

![Figure 3. Dependence of the power generated by a thermovoltaic element based on samarium sulfide on electric current.](image)

Estimates of the internal resistance \( r_{ve} \) according to the current-voltage characteristic and the dependence of power on current gave approximately the same value \( \sim 1.5 \text{ Ohm} \). The maximum power of our thermovoltaic element corresponds to the internal resistance \( R_p = r_{ve} \), equal to the internal resistance of the generator at a given temperature of the sample, as for the Seebeck effect [6].

4. Conclusion
The presented kinetic model of the thermovoltaic effect made it possible to describe the main electrophysical characteristics of energy converters based on it in classical terms and concepts of semiconductors. The experimental data obtained during the study indicate that thermovoltaic elements made on the basis of sintered polycrystalline bulk samples of samarium sulfide can be included in a standard way in electrical circuits, similarly to standard thermoelectric generators operating on the Seebeck effect. It is shown that the optimal load to obtain maximum power is equal to the internal resistance of the thermovoltaic element, as for the Seebeck effect. In this case, the internal resistance \( R_p = r_{ve} \) is the equivalent resistance of all intercrystalline necks of the sintered polycrystal, which are responsible for the current transport of electricity in the samples.

Acknowledgments
This work is supported by RFBR grant No. 19-08-00576 A.

References
[1] Golubkov A V, Goncharova E V, Kapustin V A, Romanova M V and Smirnov I A 1980 Soviet Physics, Solid State 22 2086-2090
[2] Kaminskii V V, Golubkov A V and Vasil’ev L N 2002 Phys. Solid State 44 (8) 1574-1578
[3] Kaminskii V V, Kazanin M M, Kazakov S A, Grevtsev M A and Sharenkova N V RF patent No. 2 628 677 (March 01, 2016)
[4] Myasnikov I A, Sukharev V Ya, Kupriyanov L Yu and Zav’yalov S A 1991 Semiconductor sensors in physico-chemical studies (Moscow: “Nauka” Press) p 327
[5] Bube R 1962 Photoconductivity of Solids [in Russian] (M.: Inostrannaya literature) p 558
[6] Ohotin A S, Efremov A A, Ohotin V S and Pushkarskii A S 1976 Thermoelectrical generators [in Russian] (M.: Atomizdat) p 320