The thermovoltaic effect in rare-earth semiconductors based on $SmS$ and the conversion of thermal energy into electrical energy on its basis

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Abstract. The article emphasizes the mechanism of the thermovoltaic effect in the rare-earth semiconductor material of samarium sulfide ($SmS$). The maximum achieved parameters of the $SmS$ based thermal energy converters are given. Comparison of them with the parameters of classical thermoelements proves the practicability of further developments in this field.

1. Introduction
The aim of the work was to analyze the possibilities of applying the thermovoltaic effect in rare-earth semiconductor materials based on samarium sulfide ($SmS$) for the conversion of thermal energy into electrical energy.

The thermovoltaic effect was first discovered at the Ioffe Institute of the Russian Academy of Sciences in 2000 [1, 2] in semiconductor samarium sulphide ($SmS$). It was subsequently discovered in other semiconductors: ZnO, $Pr_{0.6}Ca_{0.4}MnO_3$, Si-based structures, etc. It consists in the appearance of the electrical voltage between opposite sides of the sample while heating up to 400-500K without external temperature gradients. The value of the generated voltage on $SmS$ single crystals reached 2.5V, and in thin films it reached 4.5V. The mechanism of the effect is described in [3]. The effect is based on the fact that defective $Sm^{3+}$-ions, which create impurity donor levels, are distributed in the volume of the sample irregularly and make a certain concentration gradient. Gradient direction in this case approximately coincides with the direction of the sample’s electrodes.

2. Appearance of electrons local concentration
When the area of the sample, adjacent to one of the electrodes, is heated, a higher local concentration of conduction electrons and a gradient of n appear throughout the entire sample (‘figure 1’). Due to the diffusion of current carriers, an electric current with a density

$$j = eD \text{grad} (n),$$

appears in the sample. Here, $D$ is the electron diffusion coefficient in $SmS$. 

Figure 1. General scheme for measurement of the thermovoltaic effect.

Thus, only the mechanism of the formation of a single voltage pulse can be explained. However, the generation of pulses can continue indefinitely (‘figure 2’).

Figure 2. Generation during stationary heating of the thermoelement on the basis of thermovoltaic effect in SmS.

To explain this fact [3], it is necessary to consider the specificity of SmS band structure (‘figure 3’).

Figure 3. SmS band structure.
Semiconducting SmS has a NaCl type crystal structure. SmS can only have an n-type of conductivity. In the forbidden band at a distance of 0.23 eV there are localized 4f-levels of Sm ions. In addition, there are impurity donor levels with the position $E_i = (0.045 \pm 0.015) eV$ and concentration $N_i = 10^{20} - 10^{21} \text{ cm}^{-3}$. The impurity donor levels are connected with Sm$^{2+}$-ions, which are located not in the regular sites of samarium sublattice but, perhaps, in vacancies of sulfur one. Such defects are caused by the peculiarities of the samples creation technology.

Upon heating of the sample to a certain temperature $T_b$, a critical electron concentration $n_b$ is accumulated in the conduction band. At this moment, the Coulomb potential of the impurity Sm$^{2+}$-ions becomes completely screened and the electrons delocalize from the $E_i$-levels to the conduction band. This collective process is spasmodic and occurs primarily in the area of the sample with the maximum value of $N_i$, leading to the appearance of a high local concentration of conduction electrons $n = 10^{20} - 10^{21} \text{ cm}^{-3}$ in this area. This is the reason for the gradual increase in $\text{grad} (n)$.

3. Electric voltage pulse generation

The continuous process of electric voltage pulse generation can be presented as follows. Upon heating the sample to temperature $T_b$, the electron concentration in the conduction band grows stepwise to $n = N_i$ in the sample’s region with maximum $N_i$; consequently, the value of $\text{grad} (n)$ increases. As a result, a voltage pulse occurs. The heat absorption accompanying this pulse lowers the temperature of the sample to $T_0 < T_b$. Thus, the sample is prepared to generate the next pulse. The heater continues operating, the temperature of the sample rises to the value $T_b$ again, and the process is repeated. Figure 4 schematically shows the dynamics of temperature ($T$) and local electron concentration ($n$) in the conduction band in the sample’s area with the maximum value of $N_i$, as well as the generated voltage ($U$).

![Figure 4](image)

**Figure 4.** Scheme of the electric voltage pulses generation at the thermovoltaic effect in SmS.

Thus, we used the thermovoltaic effect in SmS to convert thermal energy into electric energy in the absence of temperature gradient. Thermoelements have been developed based on both thin film structures [4] and bulk samples. The principle of these thermoelements construction is based on the fact that bulk or film (“sandwich” type) samples consist of two layers with different concentrations of impurity donor levels. This was achieved in various ways: by diffusion, by sintering of layers with different impurity concentrations, by successive deposition of thin films of two or more materials, by
creating different values of X-ray coherent scattering regions in different parts of the sample. The conversion efficiency up to 36% was experimentally obtained [4].

4. Conclusion

A thermoelectric generator was constructed, containing a bulk sample of SmS semiconducting material, located between the metal current contacts (‘figure 5’). The method for manufacturing of thermoelectric generator comprises soldering of SmS sample to a plate of refractory metal with a metal samarium.

![Figure 5. A sample of SmS/Sm/Mo multilayer bulk structure.](image)

| Table 1. Maximum achieved results. |
|------------------------------------|
| Characteristic                     | SmS         | Classical thermoelements |
| Specific generating power, W/g     | under 1.8   | <0.2                    |
| Voltage generated by a single     | under 5     | <0.1                    |
| thermoelement, V                   |             |                         |
| Internal resistance, Ohm           | 0.2-2       | 0.2-2                   |
| Radiation resistance of electrical | 10^{10}     | 10^{9}                  |
| parameters (exposure up to the 1% |             |                         |
| change of the parameter, Roentgen) |             |                         |
| Maximum power obtained from a     | 5           | unites of W             |
| single thermoelement, mW           |             |                         |
| Transformation efficiency, %       | 36          | under 10                |

In conclusion, the use of the thermovoltaic effect in SmS looks promising for converting thermal energy into electric energy. This transformation principle has the following advantages:
1) allows conversion in the absence of an external temperature gradient;
2) allows to increase by an order of magnitude the specific power of the generated electrical signal in comparison with the classical transformation (Seebeck-effect);
3) allows to 3 times increase the conversion efficiency;
4) it allows to increase by 1-2 orders the magnitude of the electrical voltage generated by a single thermoelement;
5) can be used at low temperatures.

The disadvantage of this principle of transformation is the low power of the signal generated by a single element. This is due to the fact that only electrons that are delocalized from impurity levels participate in the generation process. To eliminate this drawback, when creating a generator, a large number of thermoelements must be plugged.

References

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