Thermal processes in SmS/Sm$_{1-x}$Gd$_x$S heterostructures at the thermovoltaic effect

S M Solov’ev, N V Sharenkova, M M Kazanin and G A Kamenskaya
Ioffe Institute, Politekhnicheskaya 26, 194021, Saint-Petersburg, Russia

e-mail: serge.soloviev@mail.ioffe.ru

Abstract. Thermal processes in SmS/Sm$_{1-x}$Gd$_x$S heterostructures are investigated. It is noted that cooling is observed on the Sm$_{1-x}$Gd$_x$S side when these heterostructures are heated. Cooling value is less than that of previously observed in SmS, but the stability is higher. It is shown that the main factor influencing the cooling effect is the collective casting of electrons into the conduction band from impurity levels. There are two multidirectional electron flows as a result of this fact - due to the thermovoltaic effect and due to the Seebeck effect.

1. Introduction
Thermovoltaic effect (TVE) is one of the new principles for converting thermal energy into electrical energy. The effect was originally detected on rare earth semiconductor SmS [1]. It was subsequently discovered in other semiconductor materials: ZnO [2], Ge, Si [3], PbTe [4] and various semiconductors of complex composition. Semiconductor samples located in a uniform temperature field without any temperature gradient and having a concentration gradient of donor levels in volume generated an electromotive force in the direction of this gradient. The nature of the effect in SmS is associated with a change in the valency of defective Sm ions located in the vacancies of the sulfur sublattice Sm$^{2+}$ → Sm$^{3+}$ + e$^-$ . The concentration of these ions in SmS is quite high $\sim 10^{20}$ cm$^{-3}$, and the activation energy in the conduction band is small (0.045±0.015 eV). In this case, the electrons pass from the 4f-levels to the conduction band and create large local concentrations of charge carriers. Such electron transitions are collective in nature. Electron transitions are accompanied by the appearance of pulses of electrical voltage and thermal processes synchronized with them. A significant decrease in the sample temperature (125 K) was found during the study of TVE [5]. The short-term cooling period is unstable, which makes it impossible to apply this cooling effect in practice.

The aim of this work is to achieve a stable and continuous cooling process. In the previous work [6] we doped SmS with europium to increase the TVE signal. When SmS is doped with gadolinium, the number of conduction electrons increases, which leads to an intensification of Sm$^{3+}$ ions ionization and their transition to the trivalent state (Sm$^{2+}$ → Sm$^{3+}$ + e$^-$). The nature of the thermovoltaic effect will change as a result of this process.

2. Samples
LnS samples, where Ln = Sm, Gd, were prepared by synthesis of simple substances Ln and S [7]. Synthesized LnS powders were taken in quantities corresponding to the required x values, mixed, briquetted, and annealed in vacuum at T = 1800 in order to prepare samples of Sm$_{1-x}$Gd$_x$S solid solutions. Two-layer heterostructures with a concentration gradient of gadolinium ions, SmS/Sm$_{1-x}$Gd$_x$S, were
prepared by combined pressing the layers of SmS and Sm$_{1-x}$Gd$_x$S powders and annealing the briquettes in vacuum at T=1800 °C for 30 min.

The composition of the samples was controlled by X-ray phase analysis.

3. Experiment

The experiments were carried out in air in a drying oven. The sample unit is schematically shown in Figure 1. It was suspended on wires inside a 35cm diameter oven. SmS/Sm$_{1-x}$Gd$_x$S Sample 6 (parallelepiped with dimensions $15 \times 6.5 \times 5.35$ mm$^3$, impurity gradient along the 5.35 mm direction) was placed between two quite massive copper plates 2. The chromel-alumel thermocouple junctions 9 were embedded in the plates. Wires 8 were attached to the plates for measuring the output signal. The sample was clamped along the 5.35mm direction. The thermocouples readings and output voltage were displayed on the analog-to-digital converter of a personal computer. The air temperature inside the oven was also monitored by a mercury thermometer.

![Figure 1. The sample unit. 1 – Insulating base of measuring cell; 2 – Movable copper contacts; 3 – Copper holders of contacts; 4 – Movable pressed contacts of spring; 5 – Insulating enamel film; 6 – Sample; 7 – Insulating enamel film; 9 – Output contacts; 9 – Two chromel–alumel thermocouples pressed against copper contacts.](image)

4. Results and discussion

SmS/Sm$_{1-x}$Gd$_x$S samples were considered. An admixture of gadolinium gives additional electrons to the conduction band, and thus facilitates the achievement of critical electron concentration that is necessary for screening the positive charge of the rest of defective samarium ions. Figure 2 shows the dependence for the SmS/Sm$_{0.9}$Gd$_{0.1}$S sample. We observe some difference in the readings of thermocouples, and on such areas the curve of output signal shows a decrease in its value. This suggests that a collective cast of electrons at one of the contacts caused a decrease in temperature in this area, which led to a decrease in the output signal. The observed value of ΔT was 33 degrees at a medium temperature of 442K. Figure 3 shows the results obtained on SmS/Sm$_{0.7}$Gd$_{0.3}$S sample. A similar picture is observed, but it is more pronounced. It is noteworthy that in both cases, just one purely thermovoltaic effect remains with a decrease in temperature. This may be due to the fact that the electrons from the conduction band do not fall back to the impurity levels collectively, but "separately," according to the reached temperature. We obtained ΔT of 77 degrees at medium temperature of 450 K in one of the next experiments (Figure 4).
Figure 2. Dynamics of the output signal and temperatures of SmS/Sm$_{0.9}$Gd$_{0.1}$S heterostructure. 1 - thermocouple on the SmS side; 2 - thermocouple on the Sm$_{0.9}$Gd$_{0.1}$S side; 3 - output signal.

Figure 3. Dynamics of the output signal and temperatures of SmS/Sm$_{0.7}$Gd$_{0.3}$S heterostructure. 1 - thermocouple on the SmS side; 2 - thermocouple on the Sm$_{0.7}$Gd$_{0.3}$S side; 3 - output signal.
Figure 4. Dynamics of the output signal and temperatures of SmS/Sm$_{0.7}$Gd$_{0.3}$S heterostructure with maximum $\Delta T$. 1 - output signal; 2 - thermocouple on the Sm$_{0.7}$Gd$_{0.3}$S side.

Figure 5. Dynamics of the output signal and temperatures of SmS/Sm$_{0.93}$Gd$_{0.07}$S heterostructure. 1 - thermocouple on the SmS side; 2 - thermocouple on the Sm$_{0.93}$Gd$_{0.07}$S side; 3 - output signal.
The concentration of conduction electrons in Sm$_1$xGd$_x$S solid solution is significantly higher than in SmS. This leads to intensification of ionization of Sm$^{2+}$ ions and their transition to the trivalent state (Sm$^{2+} \rightarrow$ Sm$^{3+}$ e$^{-}$). This process leads, on the one hand, to a change in nature of the thermovoltaic effect, and, on the other hand, to the merging of separate time intervals of temperature decrease into a single cooling process, which we observe. The mechanism of this situation is as follows: collective cast of electrons in the region near one of the contacts produces, on the one hand, a local increase in the concentration of conduction electrons, and on the other hand, a decrease in temperature due to heat absorption during cast of electrons. These two mechanisms result in the appearance of electron flows directed in opposite directions. We can see that the signal consists of two components: one is purely due to the thermovoltaic effect, and the second is due to the temperature difference formed by a mechanism similar to the Seebeck effect. Similar experiments were also carried out for SmS/Sm$_{0.93}$Gd$_{0.07}$S sample (Figure 5). Here we do not see jumps in the temperature curves, which is apparently explained by a smaller amount of gadolinium. Summarizing all the data obtained, we can conclude that the addition of europium to SmS increases the voltage of the generated signal [6]. The addition of gadolinium leads to a decrease in temperature and a cooling effect.

5. Conclusions
SmS doping with gadolinium leads to a decrease in temperature during heating due to heat absorption caused by collective transfer of electrons into the conduction band. The cooling process in the SmS/Sm$_{1-x}$Gd$_x$S heterostructures is more stable and long-lasting. Two effects with opposite direction of the electron flow work during heating of SmS/Sm$_{1-x}$Gd$_x$S heterostructures: thermovoltaic effect and Seebeck effect.

Acknowledgments
The authors are grateful to Yu V Markova for her help in this study.

References
[1] Kaminskii V V and Solov’ev S M 2001 Phys. Solid State 43 439-42
[2] Pronin I A et al. 2015 Technical Physics Letters 41 930-32
[3] Saidov A S, Leyderman A Yu and Karshiev A B 2016 Technical Physics Letters 42 725-28
[4] Kaminskii V V, Solov’ev S M, Sudak N M and Zaldastanishvili M I 2020 Technical Physics Letters 46 47-49
[5] Kaminskii V V and Solov’ev S M 2005 Tech. Phys. Lett 31 603-04
[6] Kaminskii V V, Soloviev S M, Sudak N M, Zaldastanishvili M I, Sharenkova N V and Kazanin M M 2019 IOP Conf. Series: Journal of Physics: Conf. Series 1400 066056
[7] Golubkov A V et al. Physical Properties of the Chalcogenides of Rare Earth Elements. 1976 USDOE Technical Information Center 526