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Electrical properties of solid solutions of samarium chalcogenides in the medium temperature range

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Using solid solutions of the SmS−SmSe system, we have performed studies aimed at determining the composition optimal for creating heterostructures for studying the thermovoltaic effect in the medium temperature range. The experiments have shown that solutions of $\mathrm{SmS}_{1-x}\mathrm{Se}_x$ with $0.2 \leqslant x \leqslant 0.3$ will be optimal for this purpose.

Keywords: samarium, chalcogenides, thermovoltaic effect.

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Studying the thermoelectric properties of SmS resulted in discovering in it the thermovoltaic effect (TVE) [1]. Later TVE was detected in other semiconductor materials (ZnO [2], Ge, Si [3]). TVE represents one of the new principles for converting thermal energy into electrical energy. The effect is observed in semiconductor samples located in a uniform temperature field free of any temperature gradient but exhibiting a gradient of concentration of donor levels N_i over the volume. The presence of the gradient of concentration of impurity levels N_i with activation energy of 0.04 eV over the sample volume is just what causes the presence of TVE [4]:

$$E = K \operatorname{grad} N_i, \tag{1}$$

where E is the intensity of the generated electric field. The effect coefficient K depends in a complex manner on the temperature and parameters of the semiconductor.

Studying this effect in SmS samples showed that generation of electromotive force (EMF) in SmS occurs when the sample is heated to ~ 470 K. Further heating of the SmS samples results in depletion of impurity levels. One of the ways of solution aimed at increasing the output signal based on the EMF-effect formula [5] is to deepen the donor impurity levels. In [6], the problem was solved by doping SmS with europium and ytterbium ions.

In this work, the $\mathrm{SmS}_{1-x}\mathrm{Se}_x$ solid solutions were prepared for the purpose of deepening the N_i levels. The depth of the $4f$ levels of samarium in SmSe is 0.7 eV. The increase in the energy of the $4f$ levels relative to that in SmS (0.23 eV) is caused by an increase in the crystal lattice parameter (NaCl): $a_{\mathrm{SmS}} = 5.967$ Å, $a_{\mathrm{SmSe}} = 6.200$ Å. Therefore, solid solutions of the SmS−SmSe system are also expected to exhibit deepening of impurity donor levels. An increase in the conductivity activation energy with increasing x in $\mathrm{SmS}_{1-x}\mathrm{Se}_x$ was observed earlier in [7]. The effect of the output signal increase that can occur with such deepening may be estimated by using the formula valid for non-degenerate semiconductors [6]:

$$U = \frac{k(T - T_0)}{e}\left[\frac{1}{2}\left(\ln\left(\frac{N_{i2}}{N_{i1}}\right) + \frac{E_{a1} - E_{a2}}{kT}\right)\right], \tag{2}$$

where N_{i1}, N_{i2} are the concentrations of donor levels with activation energies E_{a1} and E_{a2}, which are located in the near-contact regions, T_0 and T are the initial temperature and generation temperature.

Samples of SmX (where X = S, Se) were fabricated by synthesizing from elementary substances Sm and X [6]. Solid solutions $\mathrm{SmS}_{1-x}\mathrm{Se}_x$ (where $x = 0, 0.2, 0.3, 0.5$) were created by mixing SmS and SmSe powders taken in the amounts meeting the required values of x; after mixing, the powders were briquetted and annealed in vacuum at $T = 1600°$C. Two-layer heterostructures with a gradient of the chalcogen ions concentration ($\mathrm{SmS/SmS}_{1-x}\mathrm{Se}_x$) were prepared by pressing together the layers of SmS and $\mathrm{SmS}_{1-x}\mathrm{Se}_x$ powders and annealing the obtained briquettes in vacuum at $T = 1600°$C for 30 min. The sample compositions were controlled by X-ray phase analysis. The briquette size was $15 \times 5 \times 5$ mm.

Measurements on the samples were carried out in vacuum (for this purpose, vacuum universal post VUP-5 was used). The experimental setup layout was similar to that given in [6]. The results of measuring the resistivity of the SmS−SmSe system solid solutions are shown in Fig. 1. One can see that the depth of donor impurity levels increases with increasing content of Se in the solid solution. From the fundamentals of electronics it is known that an ideal EMF source is a source whose internal resistance is commonly assumed to be infinitesimal. The $\mathrm{SmS}_{1-x}\mathrm{Se}_x$ resistivity is $0.29\,\Omega \cdot$cm at $x = 0.2$, $1.44\,\Omega \cdot$cm at $x = 0.3$, and as high as $18.7\,\Omega \cdot$cm at $x = 0.5$. Actually, Fig. 1 demonstrates that the difference in resistance between the samples with $x = 0.2, 0.3$ and sample with $x = 0.5$ is indeed significant.

Fig. 2 presents the calculations obtained via formula (2) (curves *1–3*). One can see that the output signal magnitude is to increase with increasing x. The same figure presents the experimental results (curves *4–6*). Among the

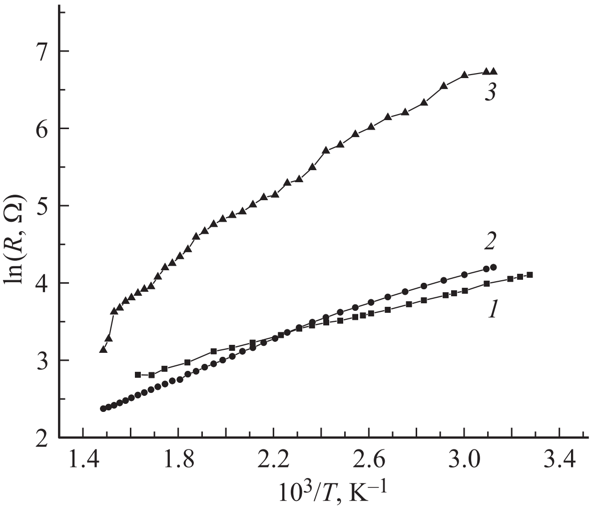

Figure 1. Temperature dependences of resistivity of solid solutions $SmS_{0.8}Se_{0.2}$ (*1*), $SmS_{0.7}Se_{0.3}$ (*2*), $SmS_{0.5}Se_{0.5}$ (*3*).

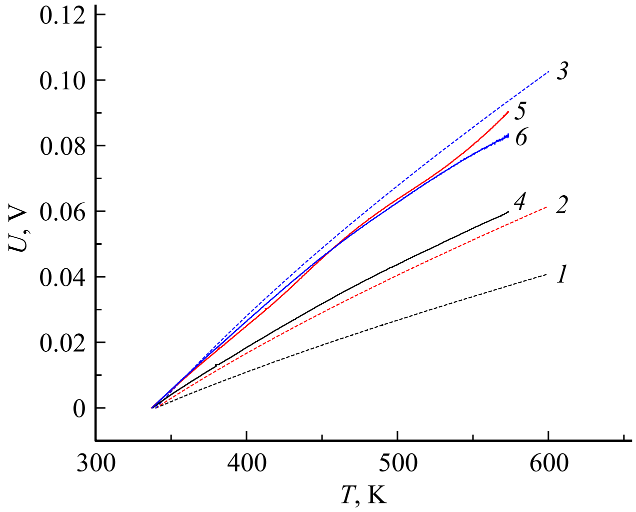

Figure 2. Calculated (*1–3*) and experimental (*4–6*) temperature dependences of the output signal of the $SmS/SmS_{1-x}Se_x$ heterostructures. $x = 0.2$ (*1, 4*), 0.3 (*2, 5*), 0.5 (*3, 6*).

presented curves, the closest to the calculated curve is the experimental curve representing measurements for $x = 0.5$ (curves *3* and *6*, respectively). At the temperature of 570 K, $U_{calc} = 92$ mV and $U_{exp} = 83$ mV. The other experimental curves have exhibited values higher than the calculated ones. This behavior can be explained by assuming that, in the process of the two-layer samples formation, distribution of their energy levels undergoes certain variations. As formula (2) shows, the logarithm of ratio between concentrations makes the lowest contribution to the output signal calculations. Hence, a greater contribution is made by the difference between the impurity levels. Apparently, levels in the solid solution have occupied a lower position during the solution formation. This is quite possible if assuming that phase compositions of the samples with $x = 0.2$ and 0.3 have changed during sintering. One of the reasons for variations in the phase composition may be the presence of oxygen in the ampoule with the sample. In this case, a portion of Sm could get oxidized during sintering, due to which the Se content in the sample could increase. However, these are technological issues that require additional studying. Another explanation could be imperfection of the thermovoltaic effect theory. Currently, efforts to develop the theory and, hence, to derive the formula for calculating the TVE output signal are being continued. Nevertheless, to date the experimental results show that the output signal generated by the $SmS_{0.7}Se_{0.3}$ heterostructure almost fully replicates the signal from $SmS_{0.5}Se_{0.5}$. Therefore, we assume that, due to high resistivity at $x = 0.5$, we have reached the maximum possible Se content in the solid solution to be used in creating a thermal-to-electrical energy converter. Thus, among the studied samples, samples with the Se content of $0.2 \leqslant x \leqslant 0.3$ are best suited for energy conversion.

In summary, we come to the following conclusions.

1. The $SmS/SmS_{1-x}Se_x$ heterostructures are indeed able to work at temperatures above 470 K.

2. Output signals of such structures are higher than those generated by previously studied SmS samples.

3. Based on the postulate of an ideal power supply and on experimental results, we have come to a conclusion that materials with $0.2 \leqslant x \leqslant 0.3$ can be optimal for the thermal-to-electric energy converters.

Conflict of interests

The authors declare that they have no conflict of interests.

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