Obtaining of SmS based semiconducting material and investigation of its electrical properties

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Semiconductor samarium monosulfide polycrystals obtained by reaction between samarium trihydride (SmH_3) and its sesquisulfide were studied. The temperature, baric and frequency dependences of the resistivity and structural features of the samples were investigated. It is shown that the value of X-ray coherent scattering region is extremely small for SmS samples, 320 Å; critical pressure of semiconductor–metal phase transition is higher than in the samples, obtained by other methods, 0.88 GPa; the temperature dependence of the resistivity has metallic behaviour. Hopping mechanism of electron transport was found. All these features are explained by more defective structure of the polycrystalline SmS samples.

In recent years samarium monosulfide (SmS) has changed from the object of basic research of its unique physical properties into the material in great demand used for manufacturing strain gauges and baroresistors, as well as thermal electrical transducers. In industrial production and in laboratory practice two basic methods are used for obtaining SmS. The first method is grounded on SmS synthesis from two elementary substances, samarium and sulphur [1], the second — on solid-phase diffusion reaction of interaction between metal Sm and its sesquisulphide (Sm_2S_3) [2]. In both cases SmS polycrystals are obtained with similar structural and electrical properties that can be varied within possible changes of synthesis parameters [1]. Later both these methods of SmS obtaining we will designate by methods 1 and 2.

The method of SmS synthesis (later — the method 3), that is grounded on the reaction between samarium trihydride (SmH_3) and its sesquisulphide, has been applied.

The α-Sm_2S_3 and SmH_3 powders were obtained from Kojundo Chemical Laboratory Co. The α-Sm_2S_3 and SmH_3 powders were mixed in a molar ratio of 1 : 1.5. A mixture was placed on a BN boat and heated at 1000°C for 3 h under a vacuum of $< 2.6 \cdot 10^{-3}$ Pa. Honeycomb Ti foil was placed on a top of the BN boat to avoid oxidation. Then the product was milled using a moter. The powder was mounted in a graphite die of 10 mm diameter and consolidated by a pulse electric current sintering (SPS-511S, Sumitomo Coal Mining Co.). The chamber of apparatus was pumped down to $7.0 \cdot 10^{-3}$ Pa. The sintering was performed at 1200°C for 1 h under the applied pressure of 50 MPa.

According to picnometer studies the samples had density ~ 5.99 g/cm^3. Compositional analysis of obtained samples made it possible to establish that they contain master phase of SmS in number of 75%, metal Sm in number of 6%, oxysulfide Sm_2O_2S in number of 8% and sesquioxide Sm_2O_3 — 11%.

Electrical parameters of the samples had the following values: resistivity $\rho = 1.4 \cdot 10^{-3}$ Ohm · cm (for the samples, obtained by methods 1 and 2, the values $(2-5) \cdot 10^{-2}$ Ohm · cm are characteristic), a conduction electrons concentration $n = 2.3 \cdot 10^{20}$ cm^{-3} at $T = 300$ K (for the samples, obtained by methods 1 and 2, the values $n = (0.5-3.5) \cdot 10^{19}$ cm^{-3} are characteristic).

Lattice distance of SmS, crystallizing in the lattice of NaCl type, according to the X-ray diffraction analysis data had the value $a = 5.971(2)$ Å that corresponds to the literature data. X-ray coherent scattering region (CSR) appeared to be equal $L = 320 \pm 50$ Å. This value is record small for SmS bulk samples. It is about two times lower than that of polycrystals, obtained by methods 1 and 2, that testify high imperfection of samples.

It is shown in [3] that the value of CSR is one of key parameters determining physical properties of crystals. For this reason it was necessary to conduct comparative studies of processes of an electrotransport in SmS samples synthesized by methods 1, 2 and 3.

Studies of temperature, baric and frequency dependences of resistance of the polycrystalline SmS samples obtained by various methods were conducted for the specified purpose. Fig. 1 presents a dependence of a resistivity on the temperature, obtained from the samples synthesized by the method 3. This dependence corresponds to metal type of conductivity ($\partial\rho/\partial T > 0$) and testifies that samples represent degenerated semiconductors.

Conduction electrons concentration has been calculated at $T = 300$ K from the data on Hall effect in tested samples, and it was $n = 2.3 \cdot 10^{20}$ cm^{-3}. This experimental fact requires separate consideration. The matter is that, according to the data on Hall effect study under pressure the value of critical concentration of free current carriers in SmS, at which a semiconductor–metal first order phase transition occurs in it, makes up $\sim 10^{20}$ cm^{-3} [4]. Thus, in the manufactured polycrystal we have overcritical conduction electrons concentration without obvious signs of

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phase transition. Reasonable explanation of the specified experimental fact can be given if we guess presence of major hopping conductivity in tested SmS samples (see below).

Under hydrostatic compression SmS samples undergo abrupt semiconductor–metal first order phase transition. In single crystals jump is strongly expressed, in polycrystals — is a little diffused. Pressure dependence of reduced electrical resistance R/R_0, where $R_0 \approx 0.22$ Ohm — resistance of the sample under normal conditions, for one of the samples is presented on Fig. 2. For comparison similar dependence of polycrystalline SmS sample, which was synthesized by methods 1 and 2 and had CSR ~ 700 Å, is given on the same figure.

The first thing that attracts attention is very high critical pressure of phase transition, 0.88 GPa, in comparison with the one that is characteristic for the samples, obtained by methods 1 and 2 — ~ 0.7 GPa.[1] Increase of phase transition pressure in more defective samples obtained by method 3, can be explained qualitatively by the fact that necessary for phase transition screening of the electrons from $4f$-levels of Sm^{2+} ions is carried out only by band electrons, which number is not so large. The electrons, participating in hopping mechanism of electrical conduction, do not screen $4f$-levels and, moreover, interfere with activations of electrons from $4f$-levels to the conduction band as they raise the level of chemical potential in the sample.

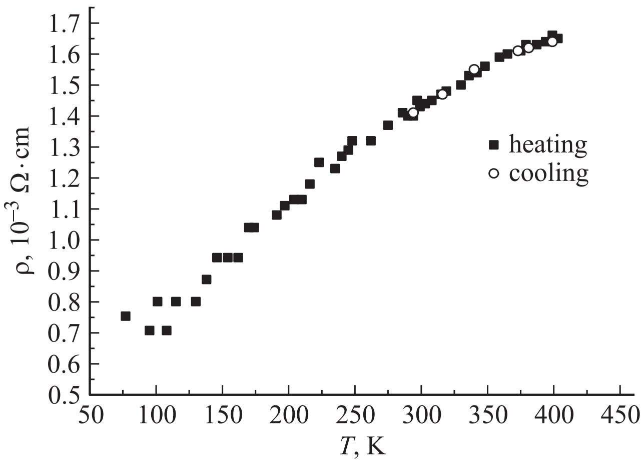

Figure 1. Temperature dependence of resistivity of polycrystalline SmS sample produced by the method 3.

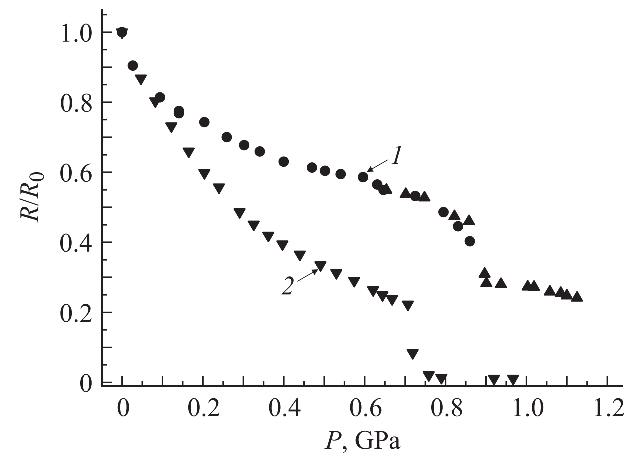

Figure 2. Pressure dependences of reduced electrical resistance of polycrystalline SmS samples: *1* — a polycrystal, obtained by method 3; *2* — typical dependence for polycrystals, obtained by methods 1 and 2.

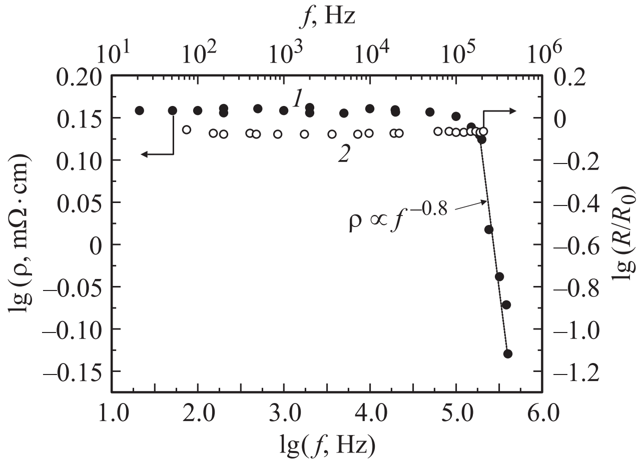

Figure 3. Dependences of logarithms of resistivity and reduced electrical resistance on frequency, obtained on SmS polycrystals by various methods: *1* — the sample, obtained by method 3; *2* — the sample, obtained by method 1 [5].

The direct proof of presence of hopping conductivity in SmS samples synthesized by method 3, has been obtained during studying frequency dependences of their resistivity ρ. Dependences of logarithms of resistivity ρ and reduced electrical resistance R/R_0 on frequency, obtained on SmS polycrystalline samples by various methods, are presented on Fig. 3. It can be seen from the figure that in sample 2, obtained by method 1, frequency dependence of electrical resistance is not observed [5]. At the same time for the sample 1, obtained by method 3, we can see classical frequency dependence of resistivity ρ: $\rho \propto f^{-0.8}$ [6].

On the basis of results of conducted comparative studies of SmS polycrystalline samples, obtained by various methods, we can come to the following conclusion. The technology of samarium monosulfide synthesis from its trihydride and sesquisulphide at the present stage of its development results in obtaining SmS samples that are strongly defective and contain considerable quantity of alien phases. It should be noted, however, that high imperfection and connected to it small values of CSR in SmS polycrystals lead to occurrence of considerable quantity of impurity donor levels $E_i = 0.045 \pm 0.015$ eV [7].

[1] For the value of phase transition pressure in polycrystalline SmS is taken such its value (rather arbitrarily), at which the absolute value of pressure derivative of sample electrical resistance $|\partial R/\partial P|$ is maximal.

Such big concentrations of such donors are unattainable at manufacturing SmS polycrystals by usual methods 1 and 2. As it is shown in [8], the gradient of concentration of these impurity levels leads to occurrence of thermovoltaic effect. Thus, application of the given procedure can be useful to obtain high gradients of E_i levels in SmS. It is possible to hope that further perfection of technology will allow to overcome the problem related to the presence of alien phases at manufacturing polycrystals by method 3.

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