

Anomalies in Young's modulus behavior after annealing in polycrystalline SmS

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Abstract: In this paper, the dependencies of Young's modulus and attenuation decrement on samarium sulfide polycrystals (SmS) under various annealing temperatures are studied by the piezoelectric ultrasonic composite oscillator technique at a frequency of 100 kHz in the temperature range of 80–300 K. A decrease in Young's modulus with an increase of the annealing temperature due to the texturing of the material was revealed. At the same time, attenuation peaks were observed at temperatures about 90 and 125 K, presumably due to Niblett-Wilks and Bordoni relaxations.

Key words: SmS; ultrasonic spectroscopy; Young's modulus; annealing in polycrystals; Bordoni relaxations; attenuation decrement

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1. Introduction

Samarium monosulfide (SmS) is one of the most studied rare-earth semiconductors, due to its unique properties, such as: record low pressure of the isostructural NaCl–NaCl semiconductor–metal phase transition (6.5 kbar at 300 K) associated with the transition of SmS to a state with an intermediate valence of samarium ion ($\text{Sm}^{2+} \rightarrow \text{Sm}^{2.7+}$)^[1, 2]; the possibility of transforming the surface layer of the sample into a metallic state by polishing^[3]; the presence of a semiconductor–metal phase transition under uniaxial compression of a single crystal^[4]; record high magnitude of piezoelectric and strain-resisting effects^[5]. In addition, the thermovoltaic effect was first discovered in this material^[6, 7], which was subsequently found in zinc oxide^[8]. Samarium monosulfide is a strain-sensitive material, based on which strain gauge sensors of various mechanical quantities are fabricated^[5, 9]. In this regard, the study of mechanical properties of SmS and, in particular, its Young's modulus (E) is of the great interest. Young's modulus is the most important technological structural sensitive characteristic, which gives information about structural changes directly from the volume of the material. It is known that in both metals and semiconductors there is a relationship between the Young's modulus and the annealing temperature in single and poly-crystals. However, an increase in the Young's modulus during annealing in single crystals is directly related to a decrease in the dislocation density, while in polycrystals there is no such straightforward interrelation. In this paper, we present the results of study of the Young's modulus and attenuation decrement temperature dependencies of

polycrystalline samarium sulfide under various annealing temperatures and we show that the abnormal behavior of the elastic and anelastic characteristics of the material is caused by the significant contribution of texturing appearing after annealing.

2. Experiment

Polycrystalline samarium sulfide was prepared by synthesis from simple Sm and S. The technology for obtaining samples includes two stages. First, the rare-earth metal Sm and chalcogen S are heated; upon reaching temperatures of 770–870 K sulfur reacts with samarium to form the Sm, SmS, Sm₃S₄, Sm₂S₃, SmS₂ phases. Heat treatment of the mixture 920–970 K leads to the thermal decomposition of SmS₂ into Sm₂S₃ and S, which, interacting with Sm, increases the yield of SmS. The obtained substance according to X-ray phase analysis is a mixture of phases, which, however, does not contain free metal and chalcogen. The second stage is high temperature annealing (1773–2273 K) obtained by briquetting bulk samples. Only after high temperature annealing do the samples become dense and well-formed. A sample with dimensions of 19.15 × 3.38 × 2.95 mm³ had the following parameters: lattice constant $a = 5.960(5)$ Å; resistivity $r = 0.03$ Ω·cm. Sample were annealed for 30 min at a temperature of 673, 913, and 1073 K in forevacuum. Then, measurements of the polycrystalline SmS were made on a DRON-3 diffractometer, Cu–K α radiation of the anode.

An acoustic technique is used as a research method. We study the Young's modulus and attenuation decrement in a wide temperature range using the three-component piezoelectric ultrasonic composite oscillator technique (PUCOT)^[10, 11] at a frequency of about 100 kHz. A single-crystal quartz rod excites a longitudinal standing wave in an oscillator. The signal from the second “gauge” quartz is used to determine the amp-

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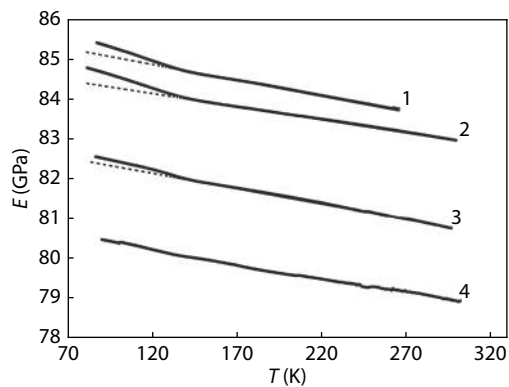


Fig. 1. Young's modulus temperature dependencies in polycrystalline SmS at various annealing temperatures: 1: without annealing, 2: 673 K, 3: 913 K, 4: 1073 K. The "step" observed at approximately 135 K in spectra 1 and 2 disappears with an increase in the annealing temperature (see spectrum 4).

litude of deformation, frequency oscillations and it maintains oscillations through the electronic feedback loop. The sample is mounted at the end of the gauge quartz. The resonant frequencies of all three elements of the system are consistent within a few percent. The size of the sample is specially selected to ensure resonance of longitudinal oscillations. For this, the sample was cut off and specially polished until a standing wave was formed in the system of the sample and quartz; i.e., the resonance of oscillations. The entire system is then loaded into a furnace or cryostat. Young's modulus was determined from the formula $E = 4\rho l^2 f^2$, where f is the oscillation frequency, ρ is the density of SmS, and l is the length of the sample.

3. Results and discussion

The results of measurements of the Young's modulus under different annealing temperatures are presented in Fig. 1. Cooling of the sample leads to the increase of the elastic modulus. However, as the annealing temperature grows, the Young's modulus decreases maintaining the general trend of spectra, Fig. 1. The drop of the Young's modulus is about several percent and reaches 6.5% at an annealing temperature of 1073 K comparing with data without annealing. At the same time the disappearance of the "step" of the Young's modulus at about 135 K with increase of the annealing temperature is noticeable, indicating stress relaxation in the structure^[12].

During annealing of metals and semiconductors, the changes of the elastic modulus occur due to the structural relaxation in the bulk of the material, which reduces the level of internal stresses, changes the size of grains and subgrains, transforms nonequilibrium boundaries into equilibrium, and leads to the gradual elimination of various defects in the crystal lattice, in particular, dislocations^[13, 14]. Due to these processes the values of the elastic modulus usually increase with annealing of the material. However, sometimes, the opposite is possible because of a certain reorientation of grains inside the crystal. A situation is possible when the grains after annealing are arranged in such a way that a certain preferential orientation of the grains appears. If the acoustic longitudinal oscillations excited in the system coincide with the predominant

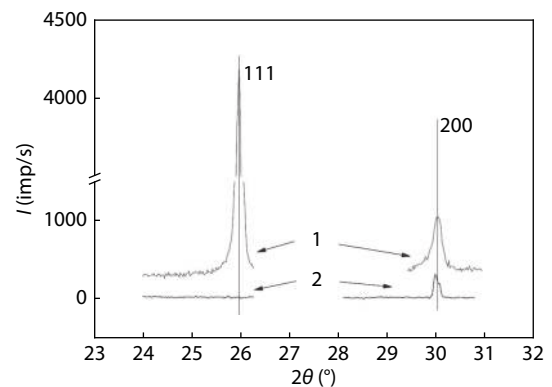


Fig. 2. X-ray diffraction patterns of the sample: 1: initial state (sample surface), 2: after heat treatment (sample cleavage). The reflection peak corresponding to plane (111) disappears after annealing; the reflection intensity peak (200) decreases twice after annealing.

crystallographic direction of the grains, for which the Young's modulus is the smallest compared to other directions in the grain. Then, in this case, the Young's modulus measured in this direction will be lower than the values obtained before annealing. Therefore, the drop of the elastic modulus during annealing is caused by texturing of the material^[15]. This texturing occurs at sufficiently high temperatures close to recrystallization point because at these temperatures the most noticeable change in grain reorientation due to their growth is observed. A great influence on this process is exerted by a strong difference of the elastic constants in different directions, as expressed by the anisotropy coefficient. In samarium sulfide the anisotropy coefficient is low ~ 0.46 ($C_{11} = 122$ GPa, $C_{12} = 11.2$ GPa, $C_{44} = 25.5$ GPa), which indicates a significant difference of the elastic constants in the main directions [111] and [200]^[16]. As a result, even partial reorientation of grains makes a large contribution to the changes of the elastic modulus, measured in the direction of longitudinal acoustic oscillations. This effect of texturing upon annealing and the subsequent drop of the Young's modulus in polycrystals had been described in detail in Ref. [8]. This change can be also seen in the diffraction patterns of the sample, Fig. 2. Diffraction patterns were obtained before annealing (curve 1) and after all stages of annealing of the sample (curve 2). At the intermediate stage of annealing at 673 K, the ratio of the peaks (111) to (200) was 3 to 1, and after annealing at 913 K it was about 4 to 3. Since, after the annealing process, the formation of $\text{Sm}_2\text{O}_2\text{S}$ and Sm_3S_4 phases is possible on the sample surface, in order to exclude the influence of these phases, the diffraction pattern for the annealed sample was registered from the cleavage, and the sample was also polished. After annealing, the reflection intensity (111) drops significantly until it completely disappears, while the reflection intensity in (200) decreases twice. In this regard, a texture appears in the [200] direction. This significant change in intensities reflects the strong influence of annealing on the orientation of grains inside the polycrystal.

According to Ref. [15] the estimation of the Young's modulus during annealing allows one to determine the transition from an isotropic to anisotropic crystal. If we assume that SmS polycrystal has a large amount of grains and their orienta-

Table 1. Young's modulus at room temperature.

Calculation	Young's modulus (GPa)
E_V	89
E_R	79,6
E_{VRH}^A	84,31
E_{VRH}^G	84,18
Without annealing	83,7
Annealing 673 K	83
Annealing 913 K	80,5
Annealing 1073 K	78,9

tions are equally probable, then it is possible to consider the material as an isotropic medium. The elastic properties of such medium can be characterized using effective elastic coefficients that relate averaged stress and strain characteristics over the entire volume^[16]. To determine the upper and lower boundaries of the Young's modulus at which the polycrystal retains its isotropy we use the Voigt (E_V) and Reuss (E_R) formulas. The arithmetic mean, E_{VRH}^A and geometric mean approximation, E_{VRH}^G were used to estimate the obtained modules:

$$E_V = \frac{(C_{11} + 2C_{12})(C_{11} - C_{12} + 3C_{44})}{2C_{11} + 3C_{12} + C_{44}}, \quad (1)$$

$$E_R = \frac{5C_{44}(C_{11} + 2C_{12})(C_{11} - C_{12})}{C_{11}(C_{11} + 3C_{44}) + C_{12}(C_{11} - 2C_{12} + C_{44})}, \quad (2)$$

$$E_{VRH}^A = \frac{E_V + E_R}{2}, \quad E_{VRH}^G = \sqrt{E_V E_R}. \quad (3)$$

Table 1 shows the theoretically and experimentally obtained Young's moduli for the SmS polycrystal. Young's modulus values at room temperature without annealing and after annealing at temperatures of 613 and 913 K are within the upper limits (Voigt criterion $E_V = 89$ GPa) and lower (Reuss criterion $E_R = 79.6$ GPa). However, the last annealing at 1073 K leads to a decrease in the Young's modulus to 78.9 GPa which is below the Reuss boundary, E_R ($E < 79.6$ GPa). Therefore, after annealing at this temperature the material can no longer be considered isotropic.

In the PUCOT method the damping (attenuation decrement) is automatically measured with the frequency. The dependencies of the attenuation decrement at different annealing temperatures in the temperature range 80–260 K were obtained (Fig. 3). As is well known, various thermally activated dislocation relaxation processes are manifested at low temperatures, such as the generation of pairs of kinks on the dislocations (overcoming the first order Peierls barrier, Bordoni peak), diffusion of single (geometric) kinks in the potential second order Peierls barrier (Niblett-Wilks peak), the interaction of dislocations with impurity pinning centers, "dragging" or "sweeping" of impurity atmospheres during the motion of dislocations and etc. Such relaxation processes are very clearly visible in the attenuation decrement spectra. There are two low temperature peaks in Fig. 3. The first peak located about 125 K is the well-studied Bordoni peak (P_2) observed in all fcc metals, and in our case in fcc semiconductor^[17]. The second peak merging with the first peak is near 90 K — the Niblett-Wilkes peak (P_1)^[18]. The micromechanism of temperature relaxation (P_1 and P_2) was proposed and examined in detail by Zeger^[19]. These thermally activated peaks are char-

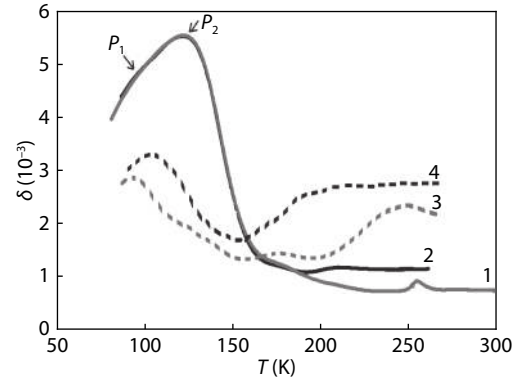


Fig. 3. Temperature dependencies of the attenuation decrement at different annealing temperatures: 1: without annealing, 2: 673 K, 3: 913 K, 4: 1073 K. Niblett-Wilks and Bordoni peaks are shown as P_1 and P_2 . Annealing of the sample leads to a disappearance of the peaks since the dislocation density decreases.

acterized by good reproducibility, as well as their disappearance or pronounced reduction during annealing at temperatures close to recrystallization, which is confirmed by the experiment. The dislocation nature of these peaks is confirmed by the "step" that appears in the temperature dependencies of the elastic modulus at ~ 135 K, Fig. 1. By comparing the spectra in Fig. 1 and Fig. 3, it can be seen that the "step" disappears (Fig. 1) with the pronounced reduction of the peaks (Fig. 3). This indicates the removal of internal stresses in the structure as a result of the drop of the dislocation density. A similar disappearance of the "step" and the reduction of the Bordoni peak is found in Ref. [12]. Such low-temperature dynamic relaxation expressed by the Bordoni peak and the observed "step" plays the role of a "switch" that switches off the dislocation source of additional deformation at low temperatures and turns it on at higher temperatures^[12]. The pronounced reduction of the P_1 and P_2 peaks indicates a decrease of the structural stresses because the dislocation density reduces after the last annealing of the polycrystal, which in turn should lead to an increase in the Young's modulus^[20]. However, the appeared texturing of the material in [200] direction makes a more significant contribution to the Young's modulus than a decrease of the density of dislocations; therefore, the Young's modulus drops, as shown in Fig. 1.

4. Conclusion

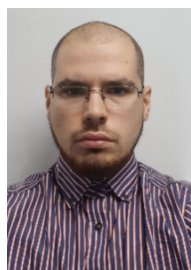
We found that the Young's modulus of SmS polycrystal is more influenced by the texturing of the material than the contribution of the dislocation processes. Thermally-activated relaxation peaks of the dislocation nature have been first detected in the SmS semiconductor. Strong decrease of relaxation peaks after heat treatment indicates the release of stresses due to a drop of the dislocation density, which in turn should lead to an increase in Young's modulus. However, due to the specific orientation of the grains during the annealing, the Young's modulus drops to values at which the material can no longer be considered isotropic. Thus, our results show that the Young's modulus changes abnormally after the annealing process. Varying the annealing temperature significantly affects the Young's modulus and allows one to change it to the necessary values required in the technological processes.

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