Investigation of the dielectric permittivity and electrical conductivity of Ce₂S₃

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The rare-earth semiconductor β-Ce₂S₃ compound samples were synthesized and their dielectric permittivity and electrical conductivity were measured in the temperature range $90-400$ K. The energy-band structure has been determined. It is shown that the long-known large electrical parameter spread of semiconductor compounds close in composition to Ce₂S₃ is explained by the structure of impurity donor levels formed by cerium atoms and ions with different ionization degrees.

It is known that cerium sesquioxides with a small deviation from stoichiometry ($Ce_{2+x}S_3$, $0 < x < 0.225$) are nondegenerate semiconductors, whose resistance at $T = 300$ K sharply decreases (by several orders) with increasing x. The concentration of conduction electrons varies in the range $(0.05-140) \cdot 10^{19}$ cm³, the electrical conductivity in the interval $0.1-55$ ohm⁻¹ · cm⁻¹, the activation energy of the conductivity from 3 to 55 meV [1]. This property of the compounds allows us to hope for the possibility of creating heterostructures with a large gradient of electrical parameters on their basis. Such structures can be used, for example, to study the thermovoltaic effect [2]. This paper is devoted to the study of electrical properties and the determination of the band structure of semiconductor samples with a composition close to Ce₂S₃.

The Ce₂S₃ powder was synthesized by the following method. It is known that the temperature of the phase transformation from tetragonal β-Ce₂S₃ with solid solution ranges from Ce₂S₃ to Ce₃S₄ into the semiconductor Th₃P₄-type cubic γ-Ce₂S₃ is 1423 ± 50 K. However, in the case of β-Ce₂S₃ containing large amounts of oxygen, oxygen acts as a stabilizer of β-Ce₂S₃ and no phase transformation occurs even if it is heated above the phase transformation temperature. The oxygen-stabilized β-Ce₂S₃ can also be expressed as $Ce_{10}S_{15-x}O_x$ ($0 \leqslant x \leqslant 1$) [3].

We considered that if the phase transformation from β-Ce₂S₃ to γ-Ce₂S₃ is reversible, β-Ce₂S₃ will be formed by introducing oxygen into γ-Ce₂S₃ at a temperature below the phase transformation temperature. In this study, we aimed to introduce oxygen while heating the γ-Ce₂S₃ powder to the phase transformation temperature, or lower, by using a pulse CVI (Chemical Vapor Infiltration) apparatus to generate β single phase.

As a starting material, commercially available γ-Ce₂S₃ powder (particle size: $7\,\mu$m) was used and oxygen was introduced using a pulse CVI apparatus. A stainless-steel cathode and anode were mounted at both ends of a reaction tube, and a porous alumina basket containing γ-Ce₂S₃ powder was placed in front of the cathode. First, the reaction tube was heated to 1473 K while applying voltage (4.5 kV) between the two electrodes. Next, an operation including, per 1 pulse, evacuation in the reaction tube (10 s), the introduction of Ar-7%H₂ gas containing O₂ (2 s), and subsequent holding (10 s) was repeated 150 times. It was assumed that, due to reversible transformation, a β-Ce₂S₃ single phase powder will be obtained.

According to the results of X-ray structural phase analysis ($\lambda_{\text{rad}} = 1.542$ Å), the synthesized powder had the following composition: Ce₂S₃-γ-phase $\approx 40\%$, Ce₂S₃-β-phase $\approx 30\%$, $Ce_{10}S_{14}O \approx 30\%$. Thus,
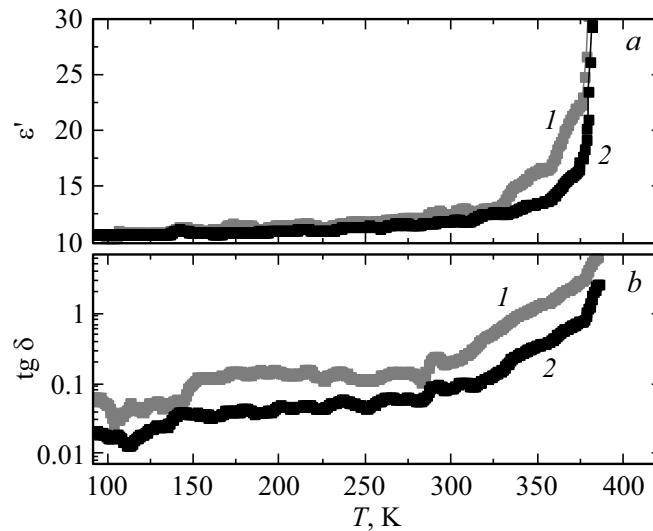
Figure 1. The temperature dependencies of a real part of permittivity (ε') and a loss tangent (tg δ). *1, 2* — measurements at frequencies, 10 and 100 kHz, respectively.

powder had a composition corresponding to the chemical formula Ce_2S_3, in which approximately every fiftieth sulfur ion is replaced by an oxygen ion. The characteristic sizes of the coherent X-ray scattering regions (CSR), D, calculated using the width of reflections by the Selyakov-Scherer formula $D = \lambda_{rad}/\cos\theta \cdot \beta$, ($\theta$-reflection angle, β-reflection widening) were about 800 Å for the γ-modification of Ce_2S_3, and 400 Å for the β-modification of Ce_2S_3 and $Ce_{10}S_{14}O$.

The Ce_2S_3 pellets of about 0.25 mm thick and 6 mm in diameter were pressed under 15 MPa. The silver electrodes were pressed into the pellets under the same pressure. The dielectric measurements were performed using the GoodWill LCR-819 impedance meter in the frequency range of $12-100$ kHz with amplitude of 1 V. Temperature dependencies of the real part of dielectric permittivity ε' and loss tangent tg δ were measured in the Ce_2S_3 pellets heated in dry nitrogen atmosphere in the temperature range of $90-400$ K at a constant rate of 3 K/min.

The temperature dependencies of the real part $\varepsilon'(T)$ of the complex dielectric permittivity $(\varepsilon^* = \varepsilon' - i\varepsilon'')$ and loss tangent tg $\delta(T)$ (tg $\delta = \varepsilon'/\varepsilon''$) are shown in Fig. 1, *a, b*. It is seen from the figure that the permittivity ε' is 11 and and is weakly dependent on the temperature in a wide range of temperatures, from 90 to 320 K. The loss tangent is also stable in the range from 140 to 320 K, but it has the frequency dependence. Above the 320 K, both values increase with increasing temperature.

The increase of the ε' and tg δ with the temperature in ceramic samples is usually associated with the Maxwell-Wagner relaxation, caused by the inhomogeneity of the dielectric [4]. In ceramics, the inhomogeneity of the dielectric medium is due to grain-grains and the boundaries between them, which differ in the permittivity ε' and the conductivity σ.

According to the Maxwell-Wagner relaxation mechanism, the permittivity increase with a temperature is determined by the thermally activated rise in the conductivity of the inhomogeneous structure, $\sigma = \sigma_0 \cdot \exp(-E_a/kT)$ (k — the Boltzmann constant and E_a — activation energy of the charge carriers).

The temperature dependencies of the real and imaginary parts of the AC conductivity $\sigma^* = \sigma' + i\sigma''$ can provide information on the activation energy of the conductivity. These dependencies according to [5,6] can be obtained from the measurements of $\varepsilon'(T)$ and tg $\delta(T)$ using the following relationships:

$$\sigma'(\omega) = \varepsilon_0 \cdot \omega \cdot \varepsilon''(\omega), \tag{1a}$$

$$\sigma''(\omega) = \varepsilon_0 \cdot \omega \cdot \varepsilon'(\omega), \tag{1b}$$

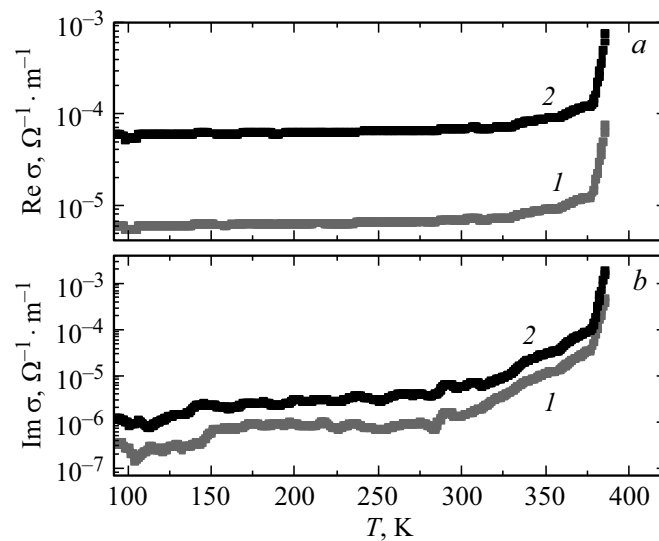$$\varepsilon'' = \varepsilon' \cdot tg\,\delta. \tag{1c}$$

Figure 2. The temperature dependencies of *a*) a real part and *b*) an imaginary part of conductivity. *1, 2* — measurements at frequencies, 10 and 100 kHz, respectively.
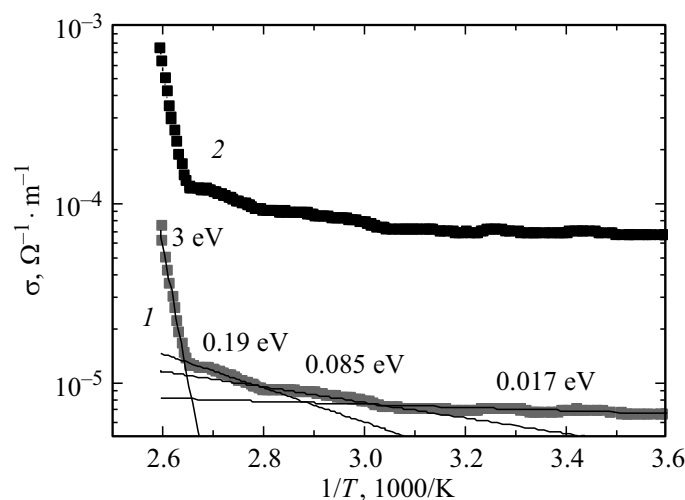

Figure 3. The temperature dependence of the real part of conductivity, constructed in the functional scale $\ln \sigma'(1/T)$. *1,2* — measurements at frequencies, 10 and 100 kHz, respectively.

The dependencies of the real part $\sigma'(T)$ and imaginary parts $\sigma''(T)$ of conductivity are presented in Fig. 2, *a, b*. The temperature dependence of the real part, plotted in the functional scale $\ln \sigma'(1/T)$, makes it possible to single out the linear that allow us to estimate the activation energy of charge carriers, E_a: 0.017, 0.085, 0.19 and 3 eV (Fig. 3).

From the obtained activation energies, one can obtain an idea of the energy-band structure of Ce$_2$S$_3$. The value of 3 eV is in agreement with the literature value of the forbidden gap Ce$_2$S$_3$, 2.6 eV [1]. Other values of activation energies can be attributed to cerium ions located outside the regular lattice sites. A similar situation occurs in SmS and EuS, where samarium and europium ions located on the boundaries of CSR create impurity donor levels of 0.045 and 0.4 eV, respectively [7,8]. This is confirmed by the results of a simple calculation, made on the basis of our data on the dielectric permeability. According to [9], the activation energies of donor levels in a semiconductor can be estimated from the relation $E_a = I/\varepsilon^2$, where I is the ionization potential of the impurity atom. Cerium atoms have second and third ionization potentials equal to 10.85 and 20.2 eV. If we assume that they are outside the regular
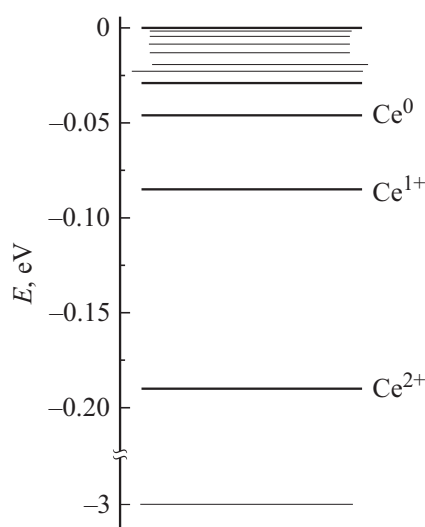
Figure 4. Energy-band structure of Ce_2S_3.

lattice sites and create donor levels, then their activation energy will be 0.09 and 0.17 eV, respectively. This approximately corresponds to the experimental activation energies of conduction electrons 0.085, 0.19 eV. The first ionization potential of cerium is 5.6 eV, which corresponds to the activation energy of 0.046 eV of donor level. The experimental value of the activation energy of conductivity 0.017 eV, probably corresponds to an activation of electrons from these levels into the tails of localized energy states, the existence of which is fully justified in [1,10]. In this case, the Ce_2S_3 energy-band structure can be represented as shown in Fig. 4.

Thus, the semiconductor material Ce_2S_3 is promising for creating heterostructures with a large gradient of electrical properties in the volume. This can be explained by the fact that the forbidden band is wide enough for electron casting through it and no processes of electrotransport through it. And the impurity donor levels responsible for electrotransport are formed by cerium atoms and ions that can be in four different ionization states and, accordingly, form the donor levels with different activation energies and electron concentrations. The degree of ionisation is very sensitive to local conditions arising during the fabrication of the sample. This explains the long-observed large dispersion of electrical parameters of semiconductor compounds based on Ce_2S_3.

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