Optimization of the functional properties in solid-state sulfide materials with the sulfur ion conductivity

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Abstract. Possibility of increasing the main functional property, the electrical conductivity in the known solid ionic salts with the conductivity of sulfur ions, by preparing composite mixtures with a semiconductor dopant is considered. The sulfide semi-product BaSm₂S₄ has been synthesized by using ceramic and chemical technology, as well as dopant ZrS₂ and composite mixtures (100–x)BaSm₂S₄-x mol.% ZrS₂ in a wide range of compositions. The study of the morphology and phase composition in the composite mixtures has revealed an ambiguous nature of the phase formation. Influence of the method for obtaining the oxide precursor on the electrical conductivity of a metacomposite based on barium thiosamarate has been investigated. The best compositional effect is achieved for metacomposites with ceramic prehistory. It is noted that in the resulting heterogeneous mixture, the sulfidic nature of the ionic salt conductivity is preserved.

1. Introduction
For the implementation of electrochemical devices (ECD) with electrodes of simple and complex sulfides, it is preferable to use solid electrolytes (SE) with the conductivity of sulfur ions. The most promising from the point of view of the existing sulfur ion transport are ternary MeLn₂S₄ sulfides (Me is an alkaline earth metal, Ln is a lanthanide), whose structural types are diverse.

Formation of phases based on ternary sulfides in any case is associated with the appearance of cationic and sulfide-anion vacancies, which can serve as ionic carriers, as well as with conduction electrons and holes. Moreover, the prevailing mechanism of defect formation depends not only on a particular alkaline earth metal layer and rare earth elements, on the size of their ions, chemical properties and structural features, but also on the temperature and partial pressures of sulfur vapor [1,2]. The calculation of ion migration channels in ST sulfides Th₃P₄, Yb₃S₄, CaFe₂O₄ showed the possibility of anion transfer and almost impossible cation migration [3].

Not so long ago, on the basis of a fairly complete study of the electrolytic properties [3-6] the existence of sulfide transfer in sulfide phases of ST, namely Th₃P₄, Yb₃S₄, CaFe₂O₄, has been proved and confirmed for ST phases of Th₃P₄ [7,8].

Despite the differences in the obtained data and its interpretation by teams from the two scientific schools, in some aspects their findings complement each other, confirming the possibility of sulfide transfer in phases based on calcium thiolantanoidates with the Th₃P₄ structure, and open up new ways of developing ideas about the class of complex sulfides, in which conductivity is carried out by sulfur ions.
However, according to the criteria for the anion transfer realization [6,9], the highest contribution to the sulfur ion transfer can be expected in crystals with the Yb$_3$S$_4$ and CaFe$_2$O$_4$ structural motifs [10]. However, their resistance, though lower than that of the Th$_3$P$_4$ ST phases, still remains rather high, which significantly hinders the use of these phases in ECDs, such as fuel cells or pumps, to change sulfur non-stoichiometry in semiconductor sulfides.

One of the methods for optimizing the functional properties of solid electrolytes is heterogeneous doping in order to increase the interfacial surfaces, which leads to the formation of additional defects and to an increase in conductivity.

In [11-16] various approaches to the choice of a heterogeneous additive have been discussed as well as the methods for producing composites with the cation and oxygen ion conductivity. The possibility of producing composite materials with the sulfur ion conductivity was first considered in [17,18] where sulfide-conducting BaSm$_2$S$_4$ (ST CaFe$_2$O$_4$), CaY$_2$S$_4$ and CaYb$_2$S$_4$ (ST Yb$_3$S$_4$) are used as ionic salts, and the layered zirconium disulfide is applied as a heterogeneous additive. However, a number of questions related to the doping of ternary sulfides with zirconium disulfide remain unanswered.

This paper discusses the possibility of optimizing the functional properties of SE by creating meta-composites based on the sulfide-conducting ionic salt BaSm$_2$S$_4$ and the semiconductor dopant ZrS$_2$, the influence of the method for preparing the oxide precursor on the electrical conductivity of the meta-composite and the effect of the dopant on the basic barium thiosamarate.

2. Experimental

The ion salt of BaSm$_2$S$_4$ was synthesized from an oxide mixture prepared by ceramic [19] and citrate-nitrate [20] methods. The oxide charge in a graphite boat in a quartz reactor was subjected to high-temperature sulfidization in a stream of purified Ar + CS$_2$ in a tube furnace of the SUOL-0.4.2/11 type (Russia). The furnace with the oxide charge was heated in a stream of argon to 1123 K. After that, the mixtures of argon and carbon disulfide were sent through a bubbler. After having reached 1373 K, the temperature was kept constant for 10 hours. To prevent desulfidization, the cooling was carried out in the stream of carbon disulfide and argon to 723 K. Then, the samples obtained were taken out in the stream of argon. The sulfide materials were preformed and homogenized by annealing. The heterogeneous ZrS$_2$ additive was obtained by sulfiding ZrO$_2$ with the similar method at temperature 1573 K.

The composite materials were obtained by mixing the ionic salt and the dopant at the given ratio, and after mechanic activation in an agate mortar, the powders were tableted at pressure of 20-30 tons/cm$^2$, and then sintered at temperature of 1273 K for 7 hours.

The phase composition of the samples was investigated by the powder X-ray phase analysis (XRD) on the XRD-7000S diffractometer (Shimadzu, Japan) (Cu K$_\alpha$-radiation). The X-ray pictures were taken at angles of $10^\circ < 2\theta < 70^\circ$ with increments of 0.02$^\circ$, exposure time of 0.6 s, with the sample rotation of 60 rpm. The phase identification was performed by using software STOE WinXPOW and Match. The chemical composition of the samples was determined by the electron microprobe analysis (EMPA). Scanning of the surface was done using microscope JEOL JSM-6510 LV (Japan), equipped with energy dispersive X-ray microanalyzer INCA X-Max (Oxford Instruments, UK), followed by mapping the samples by their elements. The thermal analysis was carried out with derivatograph DTG-60 (Japan) using the DTA and TGA methods in the aluminum oxide crucibles in air. The electrical conductivity was measured by the two-electrode method and by the impedance spectroscopy. The two-electrode method was carried out with graphite electrodes on the E7-20 immittance meter (Belarus). Temperature dependences for electrical conductivity were fixed at frequency of 100 kHz in the temperature range 445-667 K, the survey was carried out in the cooling mode. The method of impedance spectroscopy was performed with the impedance meter Z-1000 R (Elins, Russia) at isothermal exposures 573, 623, 673, 723 K in the frequency range 2 MHz-1 Hz. The results were processed using the “ZView V.2.3F” software. The transfer numbers of ions were determined taking into account the ratio of data about the total electrical conductivity and its ionic
component, determined with the method of impedance spectroscopy, and the type of ionic conductivity was estimated by the method of EMF in transfer chains with the electrodes reversible relative to the sulfide ions.

3. Results and discussion

3.1. Attestation of samples

3.1.1. Attestation of sulfide intermediates $\text{ZrS}_2$ and $\text{BaSm}_2\text{S}_4$ with different prehistory

Electronic micro-images of the sulfide intermediates are shown in figures 1, 2.

![Figure 1](image1.png)

**Figure 1.** Microimages of ionic salt $\text{BaSm}_2\text{S}_4$ with different prehistory of oxide mixture preparation: $a$ — ceramic method; $b$ — citrate-nitrate method. ×5000.

![Figure 2](image2.png)

**Figure 2.** Microimage of heterogeneous additive $\text{ZrS}_2$, ×5000.

The surface of the ion salt $\text{BaSm}_2\text{S}_4$, obtained by sol-gel method, is characterized by inhomogeneous distribution of particles, there being both small particles and large sintered areas. The surface of the base salt with ceramic prehistory, on the contrary, is characterized by more uniform distribution of particles.

Figure 2 shows the layered structure of the obtained $\text{ZrS}_2$. The results of EMPA are presented in Table 1.

The X-ray diffraction patterns of barium thiosamarate ($\text{ST CaFe}_2\text{O}_4$) with ceramic prehistory show the presence of one $\text{BaSm}_2\text{S}_4$ phase, whereas in the sample with citrate-nitrate prehistory of the oxide mixture preparation, in addition to the main component of $\text{BaSm}_2\text{S}_4$, there are small amounts of non-reacting $\text{Sm}_2\text{S}_3$ and $\text{BaS}$. The X-ray diffraction patterns of $\text{ZrS}_2$ contain only peaks of zirconium disulfide.
Table 1. Results after the microprobe analysis of sulfide intermediates

| System       | Element | Mass % of elements in sulfide intermediates |
|--------------|---------|---------------------------------------------|
|              |         | Ceramic method Real, ±0.1 | Citrate-nitrate method Real, ±0.1 |
|              |         | Theor. | Theor. |
| BaSm₂S₄      | Ba      | 25.4  | 24.3  | 15.0  | 24.3 |
|              | Sm      | 48.9  | 53.1  | 59.5  | 53.1 |
|              | S       | 25.7  | 22.6  | 25.5  | 22.6 |
| ZrS₂         | Zr      | 56.9  | 58.7  | —     | —     |
|              | S       | 43.1  | 41.3  | —     | —     |

According to EMPA the elemental composition is preserved. The results of XRD are presented in figure 3.

![Figure 3](image_url)

**Figure 3.** X-ray diffraction patterns of sulfide intermediates BaSm₂S₄ with different prehistory of oxide mixture preparation: a — ceramic method; b — citrate-nitrate method.

The results of XRD and EMPA testify to the complete sulfidization of intermediates.

3.1.2. Attestation of composite mixtures (100–x) BaSm₂S₄-xZrS₂ with chemical (x = 5, 10, 20, 30 mol.% ZrS₂) and ceramic (x = 2, 5, 10, 15, 25 mol.% ZrS₂) prehistory

According to the results of electron microprobe analysis (figure 4), the synthesized samples correspond to the given elemental composition in the cases of both citrate-nitrate and ceramic prehistory. The oxygen content in the near-surface layer is within the error of the method.

In accordance with the previously obtained [18] X-ray data, the barium thiosamarate doped with zirconium disulfide, with citrate-nitrate prehistory contains reflexes of ionic salt BaSm₂S₄, reflexes of binary sulfide Sm₂S₃ and reflexes of new sulfide phases: BaZrS₃ and Ba₂SiS₄. Silicon thiosilicate can be formed as a result of interaction between the activated with the sol-gel technology fine powder of sulfide intermediate containing BaS and the resulting silicon disulfide formed by passing sulfur carbon through a quartz reactor.

Absence of zirconium disulfide in the final product can be explained by interaction of the sulfide intermediate and ZrS₂ with formation of perovskite-like BaZrS₃, which is a sulfide-conducting solid electrolyte [21].

According to XRD (figure 5) data obtained in this work, the samples of barium thiosamarate with ceramic prehistory doped up to 10 mol.% ZrS₂, contain BaSm₂S₄ and BaZrS₃ reflexes.
Figure 4. Results from EMPA of composite materials: \(a\) — 80 mol.\% BaSm\(_2\)S\(_4\)-20 mol.\% ZrS\(_2\) with citrate-nitrate prehistory; \(b\) — 90 mol.\% BaSm\(_2\)S\(_4\)-10 mol.\% ZrS\(_2\) with ceramic prehistory.

Figure 5. X-ray diffraction patterns of heterogeneous system \((100-x)\)BaSm\(_2\)S\(_4\)-xZrS\(_2\) with ceramic prehistory, where \(x = 5\) (\(a\)), 10 (\(b\)) and 25 mol.\% ZrS\(_2\) (\(c\)).

The interaction between barium thiosamarate and zirconium disulfide, provided the amount of dopant \(x<10\) mol.\% ZrS\(_2\) leads to formation of barium thiozirconate and a solid solution (SS) of samarium sulfide in excess of the basis barium thiosamarate. According to [22], up to 10 mol.\% Sm\(_2\)S\(_3\) can be dissolved in BaSm\(_2\)S\(_4\).

\[
\text{BaSm}_2\text{S}_4 + x\text{ZrS}_2 \rightarrow x\text{BaZrS}_3 + (1-x)\text{BaSm}_2\text{S}_4-x\text{Sm}_2\text{S}_3
\] (1)
With an increase in the dopant content above 10 mol.% ZrS$_2$, new phases appear — non-dissolved Sm$_2$S$_3$, an excess of the initial dopant ZrS$_2$ and Ba$_3$Zr$_2$S$_7$ (dual perovskite).

Formation of a highly conductive layer of barium thiozirconate at the interface of the initial phases can contribute to an increase in the electrical conductivity of the synthesized composites.

Distribution of elements (Ba, Sm, S, Zr) over the surface of samples with ceramic prehistory in the system (100–$x$) mol.% BaSm$_2$S$_4$–$x$ mol.% ZrS$_2$ where $x$ = 5, 15, 25 mol.% ZrS$_2$ was investigated using the EDS method with creating maps elements. Figure 6 shows the SEM images of sintered samples, the surface of which is characterized by a fairly uniform distribution of elements such as sulfur and barium for all compositions. In addition, there are areas that are enriched with zirconium and are characterized by the complete absence of samarium, as well as areas enriched with samarium and devoid of zirconium, which confirms heterogeneity of the samples.

Taking into account the X-ray diffraction data, the regions that do not contain zirconium correspond to a solid solution of samarium sulfide in barium thiosamarate. Areas devoid of samarium are: zirconium-containing phases (BaZrS$_3$ or ZrS$_2$).

Figure 6. Microimages (mapping) of a heterogeneous mixture system (100–$x$)BaSm$_2$S$_4$–$x$ZrS$_2$, where $x$ = 5 (a) and 25 mol.% ZrS$_2$ (b).
3.2. Electrolytic properties of heterogeneous mixture (100–x) BaSm₂S₄-x mol.% ZrS₂

The temperature dependences of the electrical conductivity in samples with a sol-gel prehistory (figure 7a) are linear in the temperature range of 525-740 K under study, the activation energy of electrical conductivity being 0.6-0.7 eV [18].

![Figure 7a](image1)

**Figure 7.** Temperature dependences of electrical conductivity in systems (100–x) mol.% BaSm₂S₄-x mol.% ZrS₂: a — citrate-nitrate prehistory [20]; b — ceramic prehistory.

For samples with ceramic prehistory on the curves for temperature dependences of electrical conductivity in the high-temperature region, a kink is observed, associated with changes in the contributions of various types of conductivity to the total conductivity, which is typical of the composites having an area of low-temperature conductivity with a lower activation energy Ea on the arrhenius conductivity dependence curve [11]. The activation energy of electrical conductivity for the high-temperature region is 0.4-0.6 eV.

When comparing the concentration dependences of the electrical conductivity (figure 8), it is necessary to note different behavior of samples with chemical and ceramic prehistory.

![Figure 8](image2)

**Figure 8.** Dependence of conductivity (100–x)BaSm₂S₄-x mol.% ZrS₂ on the composition, T = 673 K.

Obviously, in the case of small dopant amounts (up to 5 mol.% ZrS₂), distributed on the activated with the sol-gel technology surface of the ionic salt, the conduction electrons of the semiconductor ZrS₂ form neutral sulfur vacancies with the charged sulfur vacancies, which arise due to the self-disordering of BaSm₂S₄, thereby reducing the ionic base salt conductivity

\[ yV^-_s + 2y\bar{v} \rightarrow yV^+_s \]  

(2)
As BaZrS$_3$ is formed, the number of the charged sulfur vacancies $V^-_S$ increases at the grain boundaries, the migration channels along the interfacial surface also increase, and the ionic conductivity becomes higher.

Ceramic preparation results in larger grains. And the formed BaZrS$_3$ is immediately localized at the interphase boundaries, increasing the electrical conductivity.

When studying the frequency dependence of the electrical conductivity of samples with ceramic history (figure 8), only one semicircle is observed on the impedance hodographs, the extrapolation of which to the $Re$ axis corresponds to the bulk resistance of the sample (R1C1 chain) [22]. The intergranular component of the conductivity failed to be determined experimentally.

**Figure 9.** Impedance hodographs at different temperatures for (100–$x$) mol.% BaSm$_2$S$_4$–$x$ mol.% ZrS$_2$, where $x$ = 0 ($a$) and 20 mol.% ZrS$_2$ ($b$).

Comparison of the data obtained by the impedance spectroscopic study and the data on the total electrical conductivity made it possible to determine the contribution of the ionic conductivity to the total electrical conductivity in the samples of the heterogeneous system (100–$x$) BaSm$_2$S$_4$–$x$ mol.% ZrS$_2$ with ceramic prehistory.

**Table 2.** Average ion transfer numbers in system (100–$x$) BaSm$_2$S$_4$–$x$ ZrS$_2$ with ceramic prehistory

| Composition, mol.% ZrS$_2$ | $T$, K | Ionic component, $10^7$ [Ω$^{-1}$cm$^{-1}$] | Electrical conductivity, $10^7$ [Ω$^{-1}$cm$^{-1}$] | $\bar{t}$ ±0.02 |
|---------------------------|--------|------------------------------------------|---------------------------------|------------|
| 2                         | 673    | 5.1                                      | 14.42                           | 0.59       |
|                           | 723    | 3.1                                      | 10.64                           | 0.97       |
| 5                         | 673    | 3.9                                      | 14.7                            | 0.41       |
|                           | 723    | 6.6                                      | 13.4                            | 0.95       |
| 10                        | 673    | 4.6                                      | 46.45                           | 0.34       |
|                           | 723    | 2.7                                      | 68.39                           | 0.33       |
| 15                        | 673    | 4.3                                      | 74.13                           | 0.18       |
|                           | 723    | 2.3                                      | 119.9                           | 0.22       |

Thus, it can be assumed that the samples containing 2-5 mol.% ZrS$_2$ in the high-temperature region are characterized as ionic conductors, whereas the samples containing from 10 to 30 mol.% ZrS$_2$ — as mixed conductors.

It should be noted that the doping of barium thiosamarate with zirconium disulfide increases the electrical conductivity of the samples with ceramic prehistory by 3 orders of the magnitude, but for the samples with the sol-gel technology — only by 2 orders of the magnitude. The same pattern is observed for the meta-composite based on CaY$_2$S$_4$.

An attempt has been made to assess whether the sulfide ion type of conductivity inherent in the BaSm$_2$S$_4$ base salt is retained in the case of heterogeneous doping with zirconium disulfide. For this purpose, the EMF has been measured in concentration chains with transfers

$$C|Fe|FeS|BaSm_2S_4|(100-x)BaSm_2S_{4-x} \text{ mol.\% ZrS}_2|FeS|Fe|C$$ (3)
and with the electrodes reversible relative to the sulfide ion [3]. In the concentration chains with transfers at the boundary of two electrolytes with different concentrations of components, a diffusion potential arises, which is associated with the numbers of ions that are not involved in the electrode processes. Sulfur ions are involved in the electrode processes of the galvanic cell (3). Therefore, the EMF of element (3) is related to the transfer numbers of all cations $E_{(3)} = f(t_{\text{Ba}^{2+}}, t_{Zr^{4+}}, t_{\text{Sm}^{3+}})$. If $E_{(3)}$ is zero, then the only current carriers are sulfur ions. At small values of the EMF, the main contribution is made by the sulfur ion conductivity, the $\text{Ba}^{2+}$ ion transfer being also present partially. The mechanism of defect formation in such system eliminates the transfer possibility for other cations, except $\text{Ba}^{2+}$ [20].

### Table 3. Value of $E_{(3)}$ (mV) for samples BaSm$_2$S$_4$–$x$ mol.% ZrS$_2$

| $x$, mol.% ZrS$_2$ | Potential $E$ at temperature K |
|-------------------|--------------------------------|
|                   | 643   | 673   | 703   |
| 2                 | 5.9   | 5.9   | 4.7   |
| 5                 | 5.9   | 5.9   | 4.9   |
| 10                | 0.5   | 0.5   | 0.4   |
| Thermal EMF       | 643-703 | 0.5   |

The measured values of the EMF in the concentration chain (3), taking into account the thermal power, suggest that the main contribution to the ionic conductivity of the studied metacomposite is made by sulfide transfer with addition of the cation transfer. For the qualitative separation of anionic and cationic transfer numbers, it is necessary to apply a modified EMF method [23]. Nevertheless, according to the results of the experiment performed, it is mainly the sulfidic transfer of the basic barium thiosamarate that is preserved in the composite mixture (100–$x$) BaSm$_2$S$_4$–$x$ mol.% ZrS$_2$.

### 4. Conclusions

Sulfide intermediates have been synthesized: the basic ionic salt BaSm$_2$S$_4$ with citrate-nitrate and ceramic prehistory of the oxide precursor preparation, the semiconductor dopant ZrS$_2$, and the heterogeneous mixture BaSm$_2$S$_4$–ZrS$_2$. According to the XRD and EMPA, the sulfidization has been complete. The XRD and SEM certification of samples (100–$x$) BaSm$_2$S$_4$–$x$ mol.% ZrS$_2$ with different prehistory has shown that with any technology for producing sulfide meta-composites, they contain a new phase — BaZrS$_3$, known as a solid electrolyte with the sulfur ion conductivity. However, the use of citrate-nitrate sample preparation leads to the contamination of the product with barium thiosilicate. The study of samples with ceramic prehistory using the EMF method with creating maps of the elements has confirmed the existence of the SS phase of samarium sulfide in the barium thiosamarate and of the zirconium-containing phases ZrS$_2$ and BaZrS$_3$.

It has been found that with an increase in the amount of dopant in the barium thiozirconate to 30 mol.% ZrS$_2$, the electrical conductivity of samples with citrate-nitrate prehistory increases by 2 orders of magnitude, passing through a minimum in the region of 5-10 mol.% ZrS$_2$, whereas the electrical conductivity of samples with ceramic prehistory increases sharply within 5 mol.% ZrS$_2$, and then increases gradually by 3 orders of magnitude compared with the basic ionic salt. The increase in electrical conductivity is most likely due to the localization of barium thiozirconate at the grain boundaries and to an increase in the migration channels for the main carriers — the charged sulfur vacancies on the interphase surfaces.

Measurement of EMF in the concentration chains with transfer and with the electrodes that are reversible relative to the sulfur ions has shown that in the composite mixture of (100–$x$) BaSm$_2$S$_4$–$x$ mol.% ZrS$_2$, the sulfide ions transfer, characteristic of the basic barium thiosamarate with addition of the cation transfer is preserved.
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