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Electrolytic properties of sulfidic ceramics on the base of calcium thiogadolinate and barium thiosamarate

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A regular research of phases on the basis of $Ca(Ba)Gd(Sm)_2S_4$–$Gd(Sm)_2S_3(BaS)$ using various electrochemical methods has been carried out. The area of solid solutions, electrolytic temperature interval, average ion transfer numbers and electron transfer numbers have been determined. The structures having the best electrolytic properties are established. The conductivity nature of solid electrolyte on the basis of barium thiosamarate and calcium thiogadolinate has been investigated. The data obtained allow to consider phases $Ca(Ba)Gd(Sm)_2S_4$–$Gd(Sm)_2S_3(BaS)$ as ionic conductors. The possible mechanism of defect formation is proposed.

Выполнено систематическое исследование фаз на основе $Ca(Ba)Gd(Sm)_2S_4$–$Gd(Sm)_2S_3(BaS)$ с применением различных электрохимических методов. Определены область твердых растворов, интервал электролитических температур, средние значения ионных и электронных чисел переноса. Определены структуры, имеющие оптимальные электролитические свойства. Исследована природа проводимости твердого электролита на основе тиосамарата бария и тиогадолината кальция. Полученные данные позволяют рассматривать фазы $Ca(Ba)Gd(Sm)_2S_4$–$Gd(Sm)_2S_3(BaS)$ как ионные проводники. Предложен возможный механизм дефектообразования.

The creation of functional ceramics with a fundamentally new conductivity type is among the main trends in the modern material science. The search for new sulfide conducting materials is based on modern criteria: realization of non-stoichiometric phases with high defect concentration; features of crystal structures with high coordination numbers of cations, capable of formation of anion-deficient phases where improvement of anion transport properties is connected with a formation possibility of heterovalent solid solutions with the same anion type and various types of cations [1]. In this connection, of great interest is a group of materials based on MLn_2S_4 (M = Ca, Ba) where La, Sm, Nd, Pr, Y, Tm, with degree of oxidation +3 are used as lanthanides (Ln) [1–4]. In this work, a complex ceramics on the basis of calcium thiogadolinate and barium thiosamarate has been synthesized. The nature of ion transfer and change of transport properties (conductivity, ion, electron transfer numbers, factors of diffusion) depending on the phase composition have been studied.

The sulfidic material were synthesized by a ceramic technique. As initial substances, CaO, $BaCO_3$ and Ln_2O_3 (special purity grade) were used. The powders (preliminary calcined at 573 K) were weighed to within $\pm 2\cdot 10^{-4}$ g and ground in an agate mortar in alcohol for one hour. The precursors were further placed in a graphite boat and loaded in a tubular reactor furnace. The synthesis was carried out in 4 stages. The following reactions took place in the reactor furnace:

$$MO + Ln_2O_3 + 2CS_2 \rightarrow MLn_2S_4 + 2CO_2 \quad (1)$$

where M = Ca,Ba; Ln=Gd,Sm.

At the first stage, the furnace was heated up to 1323 K i.e. up to the synthesis working temperature, in argon stream (at 973 K, argon stream with carbon disulfide was switched on, the flow rate being 0.3 dm^3/h). The further temperature increase is inexpedient because of the high oxygen permeability of quartz (at $T = 1323$ K).

Depending on the system, the synthesis (stage II) was carried out for 10 h for $BaSm_2S_4$ and 12 h for $CaGd_2S_4$. Then the temperature was lowered to 673 K (stage III), then the gas flow ($Ar + CS_2$) was stopped and the materials were cooled down to room temperature in argon atmosphere (stage IV). The synthesized sulfide powders were compacted into tablets and exposed to homogenizing annealing to provide more homogeneous solid samples. The annealing was carried out in the argon/carbon disulfide flow (to suppress desulfidization) for 10 hours at 1293–1323 K. The sulfidization completeness was controlled by iodometric method. The chemical analysis results of the samples synthesized allow to state that the chosen method and the mode of synthesis provide complete sulphidization of the initial oxides. The X-ray analysis of the samples was carried out using a DRON-3M diffractometer (CuK_α radiation) with scanning step of 0.10, exposure time of 2 s, the scanning range 200–600. Silicon was used as an internal standard to calculate the unit cell parameters. The complex electrical conductivity of all synthesized samples was measured by the two-electrode method with graphite electrodes using a digital measuring instrument E-7-8 in the range from room temperature up to 773 K at 10 kHz frequency. The error was 10 % of the nominal measured value.

The average ion transfer numbers were measured in a galvanic cell with the electrodes reversible with respect to sulfide ion:

$$\begin{gathered} C|Fe|FeS|Ca(Ba)Gd(Sm)_2S_4 - \\ - Gd(Sm)_2S_3(BaS)|Cu_2S|Cu|C. \end{gathered} \tag{2}$$

With gas space separated by means of high-temperature compound. The average ion transfer numbers were determined from the ratio between measured and theoretical EMF the latter being calculated taking into account the Gibbs energy for the current-inducing reaction under condition of using a hypothetical TE with $t_i = 1$ in the galvanic cell (2). The error of method is ±0.05. The electron transfer numbers were determined by the method of Hebb-Wagner [5] in an electrochemical cell:

$$\begin{gathered} C|Fe|FeS|Ca\ (Ba)Gd(Sm)_2S_4 - \\ - Gd(Sm)_2S_3(BaS)|C(+). \end{gathered} \tag{3}$$

The cell was subjected to a voltage lower than the decomposition one, in the 0 to 4 V interval at 0.05 V steps. The electron conductivity connected with the saturation electronic current corresponding to "a plateau" in the VAC curve of the cell (3) was calculated as

$$\sigma_{el} = \frac{zFl}{RTS} I, \tag{4}$$

where I is the saturation electronic current; z, the ion charge; F, Faraday number; R, universal gas constant; l and S, the geometric parameters of solid electrolyte. The electron transfer numbers were determined by Eq.(5) taking into account the complex electric conductivity:

$$t_{el} = \sigma_{el}/\sigma_{total}. \tag{5}$$

The diffusion coefficients were determined by potentiostatic chronammetry (PCA) in the cell (3) indirectly, from the current change in time at the constant potential value in the interval 723 to 773 K. The choice of material for electrodes reversible with respect to sulfur ions — Fe, FeS, is connected with the assumption about sulfidic transfer in solid electrolytes under study. The resulting current was measured as a function of time using a M-2020 microampermeter and a stop watch. For a sample of the system under study, a voltage area was chosen where the dependence $i = f(10^2/t^{-2})$ was constant, and then the current-time dependence for samples of various compositions was studied.

The diffusion coefficients ($\tilde{D}_i$) were calculated by the formula proposed by Richert [6] to find the diffusion coefficients in crystal unipolar conductors:

$$i_d = \frac{FC_0\sqrt{\tilde{D}_i}}{\sqrt{\pi t}}, \tag{6}$$

where i_d is the diffusion current, A/cm^2; F, Faraday constant; C_0 the carrier concentration; t, time, s. The diffusion activation energy was determined taking into account the temperature dependence of diffusion coefficients according to the Arrhenius equation

$$\lg\tilde{D}_i = -\frac{E}{2.3RT} + \text{const.} \tag{7}$$

The samples of systems $CaS–Gd_2S_3$, $BaS–Sm_2S_3$ in the range composition close to probable ternary compound were certified by the RPA method.

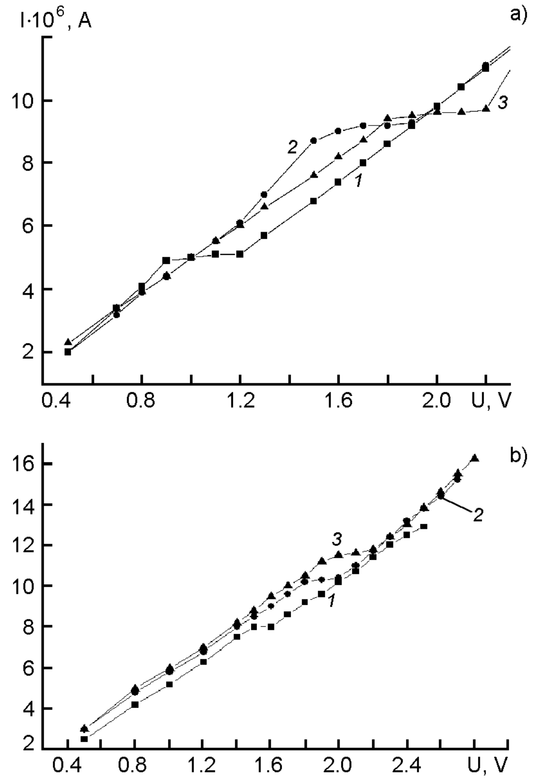

Fig. 1. Volt-ampere dependence for a cell: a) (-) C|Fe|FeS|BaSm$_2$S$_4$ – x mol. % Sm$_2$S$_3$|C (+); b) (-) C|Fe|FeS|CaGd$_2$S$_4$ – x mol. % Gd$_2$S$_3$|C (+).

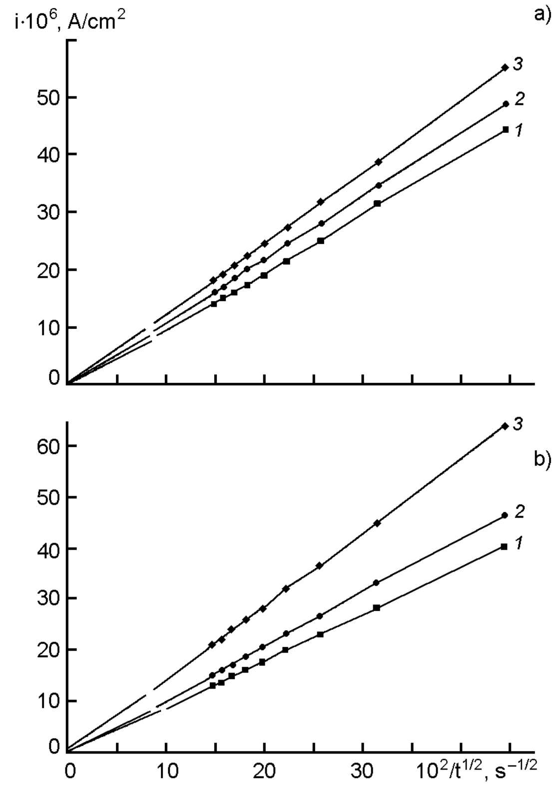

Fig. 2. Dependence of current density on $10^2/\sqrt{t}$ for samples of structures: a) BaSm$_2$S$_4$ – 4 mol. % Sm$_2$S$_4$; b) BaSm$_2$S$_4$ – 4 mol. % BaS. *1* — T = 673 K; *2* — T = 693 K; *3* — T = 713 K.

The synthesized stoichiometric samples of system (1–x)CaS–xGd$_2$S$_3$, according to X-ray analysis, show reflections from the single phase CaGd$_2$S$_4$, crystallized in the cubic lattice of Th$_3$S$_4$ type [7]. The area of solid solutions in this system on the side of excess alkali-earth metal (AEM) sulfide is insignificant and extends up to CaS molar fraction 0.49 while being extended enough, up to molar fraction 0.60, from the side of Gd$_2$S$_3$. The X-ray phase analysis of the synthesized samples of (1–x)(Ba)S–x(Sm$_2$S$_3$) system where Sm$_2$S$_3$ molar fraction x = 0.47–0.53 has shown presence of the single phase BaSm$_2$S$_4$ which crystallizes in a spinel type structure. The X-ray diffraction (XRD) patterns of samples where molar fraction of Sm$_2$S$_3$ $x < 0.47$ and $x > 0.53$ contained reflections from the second phase: barium sulfide and samarium sulfide, respectively. This fact allows to consider that as a result of synthesis, ternary compound BaSm$_2$S$_4$ was formed with bilateral area of solid solutions of binary sulfides BaS and Sm$_2$S$_3$ on its basis. The XRD patterns of barium thiosamarate samples alloyed with samarium sulfide after homogenizing annealing in CS$_2$ atmosphere contain reflections from stoichiometric BaSm$_2$S$_4$ in a wider area of structures. The homogenizing annealing obviously increases the solubility of binary sulfides in the ternary one, expanding the borders of the homogeneity area. Thus, the synthesized samples can be presented as phases BaSm$_2$S$_4$–xSm$_2$S$_3$ and BaSm$_2$S$_4$–yBaS (where x varies from 0 to 14 mol. %, and y from 0 up to 12 mol. %).

The temperature dependence of complex electric conductivity was studied within the temperature range 293 to 773 K. For samples of all compositions in the systems under study, a jump-like increase in the slope of $\lg\sigma = f(1/T)$ dependences is observed within the temperature range 600–650 K. Such change in slope can be connected with the change of contribution from ionic conductivity to the total one.

Ionic conductivity in stoichiometric barium thiogadolinate and thiosamarate is revealed at higher temperatures than in phases on their basis. This is well agreed with the idea about electron conductivity formation in CaGd$_2$S$_4$ and BaSm$_2$S$_4$ due to thermal dissociation. The shift of electrolytic interval in solid solutions of Gd(Sm)$_2$S$_3$ in Ca(Ba)Gd(Sm)$_2$S$_4$ to-

Table 1. Transfer numbers for TE of system $BaSm_2S_4$ — x mol. % Sm_2S_3 (BaS) and $CaGd_2S_4$ — X mol. % Gd_2S_3

X мол. % BaS, Sm_2S_3	T = 673 K		T = 693 K		T = 713 K	T = 723 K
	$t\bar{e}\cdot10^3$	$\bar{t}_i\pm0.05$	$t\bar{e}\cdot10^3$	$\bar{t}_i\pm0.05$	$t\bar{e}\cdot10^3$	$\bar{t}_i\pm0.05$
$BaSm_2S_4$ – x моль. % BaS						
$x = 0$	5.814	0.70	5.220	0.70	2.243	0.70
2	0.465	0.97	0.318	1.00	0.174	1.00
4	0.207	0.97	0.124	0.98	0.065	1.00
6	4.312	0.93	5.544	0.95	2.109	0.98
10	3.054	0.80	2.845	0.82	1.931	0.84
14	–	0.72	–	0.74	–	0.77
$BaSm_2S_4$ – x моль. % Sm_2S_3						
$x = 0$	5.814	0.70	5.220	0.70	2.243	0.70
1	–	0.96	–	0.98	–	1.00
2	0.300	0.99	–	1.00	–	1.00
4	0.029	1.00	0.023	1.00	0.022	1.00
6	0.087	0.97	0.075	1.00	–	1.00
8	0.263	0.99	0.118	1.00	0.044	1.00
10	0.743	0.80	0.963	0.82	0.674	0.86
14	–	0.80	–	0.81	–	0.83
20	–	0.79	–	0.82	–	0.84
$CaGd_2S_4$ – x мол. % Gd_2S_3						
	673 K		693 K		723 K	
	$\bar{t}_i+0.05$	$t_e\cdot10^4$	$\bar{t}_i\pm0.05$	$t_e\cdot10^4$	$\bar{t}_i\pm0.05$	$t_e\cdot10^4$
$x = 0$	0.80	1.89	0.7	2.00	0.7	2.41 ^
1	1.0	1.34	1.0	1.50	1.0	1.22
2	1.0	0.32	1.0	0.35	1.0	0.38
4	1.0	0.15	1.0	0.18	1.0	0.36
6	1.0	0.10	1.0	0.10	1.0	0.20
8	0.9	0.10	0.9	0.16	0.9	0.20
12	0.9	0.20	0.9	0.60	0.8	0.74
20	0.9	0.80	0.9	0.90	0.8	1.70

ward lower temperatures is well explained by increase in concentration of ionic defects in the course of doping. The conductometric data have allowed to estimate the area of solid solutions and are well agreed with the XPA data.

The average ion transfer numbers obtained by EMF method are presented in Table 1. The analysis of the data allows to consider the phases of $CaGd_2S_4$ — (1–6) mol. % Gd_2S_3 composition to be ion conductors with high enough average ion transfer numbers. The solid solutions based on $BaSm_2S_4$ containing 1–4 mol. % Sm_2S_3 and 1–6 mol. % BaS are practically ion conductors with $\bar{t}_i = 1.0$. At the alloying additive of binary sulfides exceeding 6 mol. % $Gd(Sm)_2S_3$, the average ion transfer numbers decrease.

The general shape of the VAC obtained when determining the electron transfer numbers at temperatures 673, 693, 713 K for samples of various systems is the same (Figs. 1a, b). As it is seen from the Figure, the saturation electronic current corresponding to zero slope of $I = f(U)$ dependence increases regularly as the temperature rises. This could be explained by the capability of the researched sulfides to lose sulfur easily at high temperature due to thermal dissociation, which may result in a deviation from stoichiometry towards the excess of metal and to appearance of electron conductivity as a result of the metal ionization accompanied by transition of electrons into the conductivity band. Basing on the saturation electronic current electron transfer numbers (Table 1) have been calculated. When discussing the results of electronic conductivity research, it is to note that the use of graphite as a blocking electrode results in the overestimated values of elec-

Table 2. Effective factors of diffusion, self-diffusion and energy of diffusion activation of sulfide ion in system $CaGd_2S_4$ — x mol. % Gd_2S_3

Structure x mol. % Gd_2S_3	D_e, at T, T_o			$\tilde{D}_i$, at T, T_o			E_{De}, eV
	673	693	713	673	693	713	
0	$1.88{\cdot}10^{-12}$	$2.64{\cdot}10^{-12}$	$3.48{\cdot}10^{-12}$	$4.52{\cdot}10^{-14}$	$4.88{\cdot}10^{-14}$	$4.41{\cdot}10^{-14}$	0.65
2	$3.92{\cdot}10^{-9}$	$4.43{\cdot}10^{-9}$	$4.89{\cdot}10^{-9}$	$3.48{\cdot}10^{-11}$	$3.175{\cdot}10^{-11}$	3.4810^{-11}	0.24
3	$8.74{\cdot}10^{-10}$	$9.31{\cdot}10^{-10}$	$1.34{\cdot}10^{-9}$	$3.85{\cdot}10^{-11}$	$3.85{\cdot}10^{-11}$	$5.37{\cdot}10^{-11}$	0.18
6	$1.81{\cdot}10^{-9}$	$1.95{\cdot}10^{-9}$	$2.15{\cdot}10^{-9}$	$5.60{\cdot}10^{-11}$	$7.69{\cdot}10^{-11}$	$5.60{\cdot}10^{-11}$	0.17
10	$7.84{\cdot}10^{-10}$	$9.04{\cdot}10^{-10}$	$1.05{\cdot}10^{-9}$	$2.59{\cdot}10^{-11}$	$4.36{\cdot}10^{-11}$	$15.03{\cdot}10^{-11}$	0.31
16	$1.51{\cdot}10^{-10}$	$1.74{\cdot}10^{-10}$	$1.79{\cdot}10^{-10}$	$1.13{\cdot}10^{-11}$	$1.48{\cdot}10^{-11}$	$0.83{\cdot}10^{-11}$	0.24
20	$7.77{\cdot}10^{-11}$	$9.15{\cdot}10^{-11}$	$1.03{\cdot}10^{-10}$	$9.33{\cdot}10^{-13}$	$8.88{\cdot}10^{-13}$	$11.24{\cdot}10^{-13}$	0.29

tron transfer numbers. Therefore, the electrolytic properties of the TE are better and the true contribution of electron (not hole) conductivity is lower than it follows from the data by the Hebb-Wagner method ($t_e \le 10^{-4}$).

When performing the chronammetric research, the voltage range (1.8–2.2 V) was chosen where the processes taking place in cell (3) corresponded to the diffusion kinetics. Fig. 2 shows the isothermal chronammetric dependences for the samples of phases based on $BaSm_2S_4$ and Fig. 3 – shows the chronammetric curves for samples of system $CaGd_2S_4$ – x mol. % Gd_2S_3. The diffusion coefficients and the activation energies of the related diffusion calculated under account for slope of the straight lines by equations (6, 7) for crystals $CaGd_2S_4$ and phases on its basis are given in Table 2 as well as the self-diffusion coefficients and activation energies calculated using the results of conductometric research by the Einstein equation

$$D_e = f\frac{\sigma \bar{t}_i T K}{C_o}, \qquad (8)$$

where $K = k/Ne^2$; D_e, self-diffusion coefficient, cm^2/s; σ, complex electric conductivity, Ω^{-1} cm^{-1}; T, temperature, K; C_0, concentration of current carriers, mole/cm^3; k, Boltzmann constant, J/K; N, Avogadro number, mole^{-1}; e, the electron charge, C; $\bar{t}_i$, ion transfer numbers; f, a correlation factor supposed to be 1 at the first approximation.

The self-diffusion and effective diffusion coefficients vary in the same manner as the super-stoichiometric contents of Gd_2S_3 increases but differ in absolute size. The self-diffusion coefficients exceed by 2–2.5 times the effective diffusion ones for the major carrier. Such a ratio, according to [8], is possible in case of heavily disordered lattice with higher concentration of vacancies which, due to the interaction, may result in formation of associates and in reduction of effective diffusion coefficients for the major carrier.

Basing on the results obtained by conductometry, EMF, Hebb-Wagner and PCA mrthods, the isothermal dependences of electrolytic properties of calcium thiogadolinate and barium thiosamarate on the super-stoichiometric impurity content have been investigated. The isothermal dependences of all properties investigated on the composition of the investigated systems near the stoichiometric compounds (Figs. 4, 5) are at the first glance similar to the solid sulfide conducting electrolytes in systems $CaS–Sm_2S_3$, $CaS–Nd_2S_3$ [1–4], and are well described by the vacancy mechanism of defect formation.

$$BaS(\rightarrow BaSm_2S_4) \longleftrightarrow \qquad (9)$$
$$\longleftrightarrow Ba^{*}_{Ba} + S^{*}_{S} + 2V^{3-}_{Sm} + 3V^{2+}_{S},$$

$$Sm_2S_3(\rightarrow BaSm_2S_4) \longleftrightarrow \qquad (10)$$
$$\longleftrightarrow 2Sm^{*}_{Sm} + 3S^{*}_{S} + V^{2-}_{Ba} + V^{2+}_{S},$$

$$Gd_2S_3(\rightarrow CaGd_2S_4) \longleftrightarrow \qquad (11)$$
$$\longleftrightarrow 2Gd^{*}_{Gd} + 3S^{*}_{S} + V^{2+}_{S} + V^{2-}_{Ca}.$$

The character of changes in all properties depending on the composition is identical for both researched systems in the excess sulfide area. The maximum values of electron transfer numbers, electric conductivity activation energies and diffusion coefficients correspond to the stoichiometric compounds, where defects may be formed

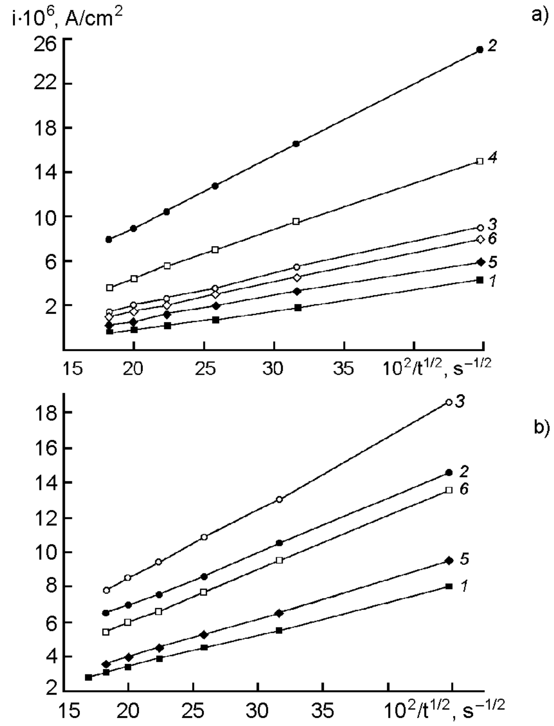

Fig. 3. Chronoammetric direct cells (-) C|Fe|FeS|CaGd$_2$S$_4$– x mol. %Gd$_2$S$_3$|C (+) for various x (*1* — $x = 0$; *2* — $x = 10$; *3* — $x = 16$; *4* — $x = 20$; *5* — $x = 2$; *6* — $x = 6$) at temperatures: a) 673 K; b) 693 K.

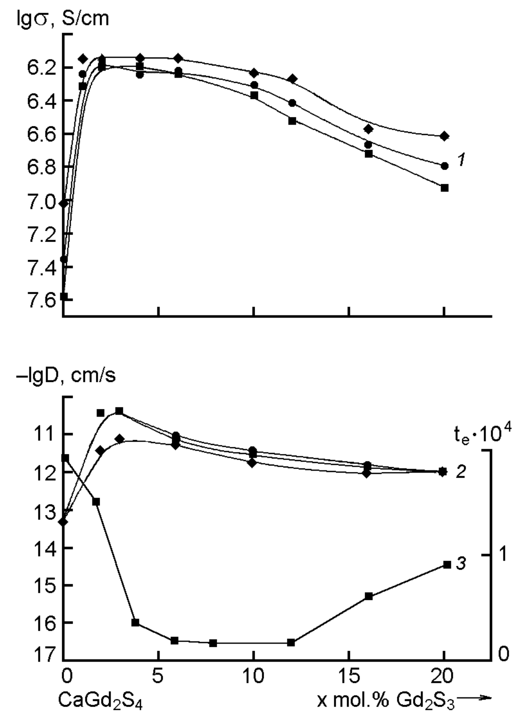

Fig. 4. Isothermal dependence structure — property of system CaGd$_2$S$_4$–x mol. % Gd$_2$S$_3$. *1* — electric conductivity, *2* — factors of diffusion, *3* — electronic numbers of transfer.

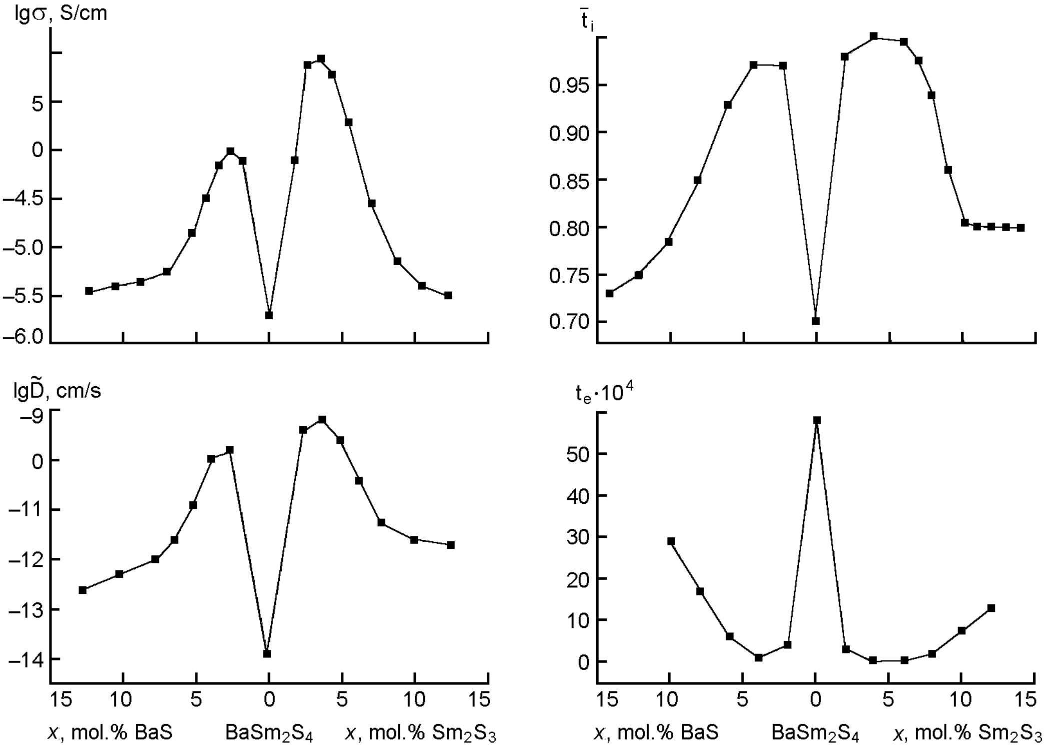

Fig. 5. Dependence structure property of system BaSm$_2$S$_4$ — x mol. % Sm$_2$S$_3$ (BaS) at = 673 K.

both as a result of self-disordering according to Shottky and due to the exit of sulfur into the gas phase as a result of thermal dissociation. As the quantity of ionic defects in self-disordering is insignificant, the occurrence of electron carriers due to thermal dissociation influences considerably the complex conductivity (reduction of contribution from ion conductivity).

Maximum electric conductivity, t_i and diffusion coefficients correspond to the phases formed at dissolving 1–6 mol. % BaS and 1–4 mol. % Sm_2S_3 in $BaSm_2S_4$ and from 1 to 6 mol. % Gd_2S_3 in $CaGd_2S_4$. It is obvious that the quantity of double-ionized (at A-EM and sulfur or at R-EM and sulfur) vacancies formed herewith correspond to the concept of "diluted solution" [8], where the mobility of ions is maximum, and consequently, average ion transfer numbers, electric conductivity and diffusion coefficients are maximal as well. The low mobility of A-EM and R-EM cations in this case is probably connected with the fact that the sizes of migration channels for the A-EM and R-EM ions in the ternary sulfide structure are smaller than the interval energetically favorable to carry these cations.

A further increase in concentration of alloying additives from 6 to 10 mol. % BaS, from 4 to 10 mol. % Sm_2S_3 and from 6 to 10 mol. % Gd_2S_3 results in reduction of electrolytic properties due to formation of neutral $[V_{Me}^{2-}V_S^{2+}]$ or charged $[V_S^{2+}V_{Ln}^{3-}]$ associates [9]. In the field of composition close to the edge of solid solution area (from 10 to 14 mol. % of binary sulfides in system $BaSm_2S_4$ - mol. % Sm_2S_3 (BaS) and for samples with the content more than 10 mol. % of gadolinium sulfide in system $CaGd_2S_4$ – x mol. % Gd_2S_3), the properties depend on the structure weakly. The constant values of average ion and average electron transfer numbers allow to judge the achievement of the solid solution edge and the transition to a biphase system. The work has been supported by the grant of the Russian Federal Property Foundation No.05-03-33188.

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Електролітичні властивості сульфідної кераміки на основі тіогадолінату кальцію та тіосамарату барію

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Виконано систематичне дослідження фаз на основі $Ca(Ba)Gd(Sm)_2S_4$–$Gd(Sm)_2S_3(BaS)$ з застосуванням різних електрохімічних методів. Визначено область твердих розчинів, інтервал электролітичних температур, середні значення іонних та електронних чисел переносу. Визначено структури, що мають оптимальні електролітичні властивості. Досліджено природу провідності твердого електроліту на основі тіогадолінату кальцію та тіосамарату барію. Одержані дані дозволяють розглядати фази $Ca(Ba)Gd(Sm)_2S_4$–$Gd(Sm)_2S_3(BaS)$ як іонні провідники. Запропоновано можливий механізм дефектоутворення.