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Thermodynamic characteristics of ternary sulfides MLn_2S_4 and solid solutions thereof

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Thermodynamic characteristics of ternary sulfides MLn_2S_4 and solid solutions thereof have been determined by EMF method in various modifications. The research results have shown that solid electrolytes $CaGd_2S_4$ and $BaTm_2S_4$ are stable compounds within the electrolytic range 653–723 K. The simultaneous determination of the binary sulfide activity in ternary $BaTm_2S_4$, CaY_2S_4, $CaSm_2S_4$, $CaPr_2S_4$ systems and of the cation and anion transfer numbers allowed us to estimate the phase stability limits and to propose a vacancy mechanism of defect formation and suggest the predominantly sulfide-ion type conductivity in the solid electrolytes studied.

Методом ЭДС в различных модификациях определены термодинамические характеристики тернарных сульфидов MLn_2S_4 и твердых растворов на их основе. Проведенные исследования позволили считать твердые электролиты $CaGd_2S_4$ и $BaTm_2S_4$ устойчивыми соединениями в электролитическом интервале 653–723 К. Одновременное определение активности бинарных сульфидов в тернарных $BaTm_2S_4$, CaY_2S_4, $CaSm_2S_4$, $CaPr_2S_4$ и катионных и анионных чисел переноса сделало возможным оценить границы устойчивости фаз, предложить вакансионный механизм дефектообразования и преимущественно сульфид-ионный тип проводимости в исследуемых твердых электролитах.

Ternary sulfides MLn_2S_4 (M is Ca, Ba; Ln is La, Y, Nd, Pr, Sm, Tm) are extensive defect phases with a probable vacancy mechanism of defect formation [1], and are of interest as potential sulfide solid electrolytes [2, 3]. To understand in more detail the ion transfer processes in these solid electrolytes, it is necessary to determine a number of thermodynamic parameters characterizing formation peculiarities of the solid solutions based on MLn_2S_4 ternary compounds having the best prospects from the ion transport point of view.

The studied solid electrolytes were synthesized using the high-temperature solid state reactions from appropriate amounts of MCO_3, Ln_2O_3, CS_2 in argon atmosphere (T = 1320 K, τ = 12 h) [1, 2]. The data of the micro-X-ray spectroscopic analysis for S^{2-}, M^{2+}, Ln^{3+} and the X-ray diffraction results (DRF 2.0 diffractometer, filtered iron radiation) [4–7] have evidenced formation of orthorhombic $BaLn_2S_4$ phases ($CaFe_2O_4$ type structure), $CaLn_2S_4$ compounds (Th_3P_4 type cubic structures and Yb_3S_4 type orthorhombic structures) and of phases on their basis in all obtained systems. The electrolytic properties of MLn_2S_4 compounds and of phases based thereon were studied using conductivity [1,2,4,7], EMF [2, 4, 5], Tubandt [8], and Hebb-Wagner [1, 6, 7, 9] methods.

Studies in formation thermodynamics of ternary sulfides MLn_2S_4 from binary MS and Ln_2S_3 carried out in this work have provided thermal stability estimation for the basic sulfides within the electrolytic temperature range. Comparing the variation regularities of electrolytic properties studied and also of thermodynamic characteristics of ternary MLn_2S_4 doped with binary sulfides has allowed us to determine the phase stability limits, to make a conclusion about the nature of the major carriers and to offer a possible mechanism of defect formation in the studied sulfide containing systems.

Thermodynamics of MLn_2S_4 ($CaGd_2S_4$ and $BaTm_2S_4$) ternary sulfides formation from binary MS and Ln_2S_3 (Ca(Ba)S and $Gd(Tm)_2S_3$) was studied using EMF method in concentration chains:

$$C/Cu/Cu_2S/Ln_2S_3 - MLn_2S_4/MS - MLn_2S_4/Cu_2S/Cu/C \quad (1)$$

with electrodes reversible with respect to sulfur ions.

When there is no electron conductivity, the EMF of chain (1) (at $t_e \to 0$), according to [10], is:

$$E = \frac{1}{6F}\int_{\mu_{MS}}^{\mu_{MS}} (3t_{S^{2-}} - t_{Ln^{3+}})d\mu_{MS}. \quad (2)$$

The current inducing reaction is:

$$MS + Ln_2S_3 \to MLn_2S_4. \quad (3)$$

The free energy of this reaction is connected with EMF of cell (1) by well known relationship:

$$\Delta G = -6FE. \quad (4)$$

The thermodynamics of reaction (3) was studied using solid solutions of various concentrations. The well reproducible EMF values were obtained only for solutions with the concentration of binary sulfides no more than 2 mol %. In solid solutions of higher concentration, the EMF values in parallel experiments were irreproducible, that is connected most likely with formation of associates of charged defects reducing the efficiency of ion transfer. The dissolution thermodynamics of binary sulfides in ternary thiolanthanates was studied by EMF method using several concentration galvanic cells (the Chebotin and Obrosov method) [11]. This method makes it possible to determine simultaneously the activity of admixture in a compound and to subdivide the ionic constituent of conductivity into the cationic and anionic ones.

The experiments were carried out in galvanic cells of the type:

$$C|M|MLn_2S_4 - xLn_2S_3(MS)|MLn_2S_4|M|C, \quad (5)$$

$$C|Fe|FeS|MLn_2S_4|MLn_2S_4 - xLn_2S_3(MS)|FeS|Fe|C \quad (6)$$

in the atmosphere of purified argon, in temperature range 650 to 750 K (x is the mole fraction of doping binary sulphide). As the electrodes of cell (5) are chemically active, the EMF was measured by an instantaneous touch [12].

Both the EMF of the cell (5) with electrodes reversible with respect to the metal cations (E_M) and the diffusion potential in this cell are connected with the transport numbers for sulfide ions and rare-earth metal (REM) ions. The EMF of cell (6) where the electrodes are reversible with respect to sulfide-ion (E_S) is connected with the transport numbers for the metal and lanthanide ions. In the case of alloying a ternary compound by a sulphide of REM, vacancies in the sulphur and calcium sublattices are expected to be mobile. On the other hand, in the case where the alloying component is MS, the charge carriers are ions of sulphur and lanthanide [1]. The method we employed makes it possible to determine transport numbers for ions at an accuracy of ±0.01, provided the obtained data are statistically significant.

Changes of electrolyte concentration in near electrodes rm are known to be related to EMF [1, 11, 13] as:

$$\tau_M = \frac{1}{1 - \frac{dE_S}{dE_M}}, \quad (7)$$

$$\tau_S = \frac{1}{1 - \frac{dE_M}{dE_S}}. \quad (8)$$

The concentration changes for solid solutions Ln_2S_3 in MLn_2S_4, in turn, are connected with ion transport numbers by relations:

$$t_{M^{2+}} = -\tau_S, \quad (9)$$

$$t_{S^{2-}} = \tau_M \quad (10)$$

and for solid solutions MS in MLn_2S_4, by relations:

$$t_{Ln^{3+}} = -\tau_S, \quad (11)$$

$$t_{S^{2-}} = \tau_M - \frac{t_{Ln^{3-}} \cdot q_S^2}{q_{Ln}(q_{Ln} + q_M)} \quad (12)$$

where q is the correspondingion charge.

It has been shown [10, 11] that the chemical potentials of the cells (5) and (6) are relater to the chemical potential of Ln_2S_3 dissolution as

Table 1. Thermodynamic characteristics of $CaS + Gd_2S_3 \rightarrow CaGd_2S_4$ reaction

	T, K				
	653	673	693	713	723
E±0.5, mV	11.5	13.8	16.0	17.3	18.5
$-\Delta G$±0.1, kJ/mole	6.7	8.0	9.3	10.0	10.7
ΔS ±0,11, J/(mole·K)	46	46	46	46	46
ΔH ± 0.5, kJ/mole	23.3	23.0	22.7	22.8	22.7

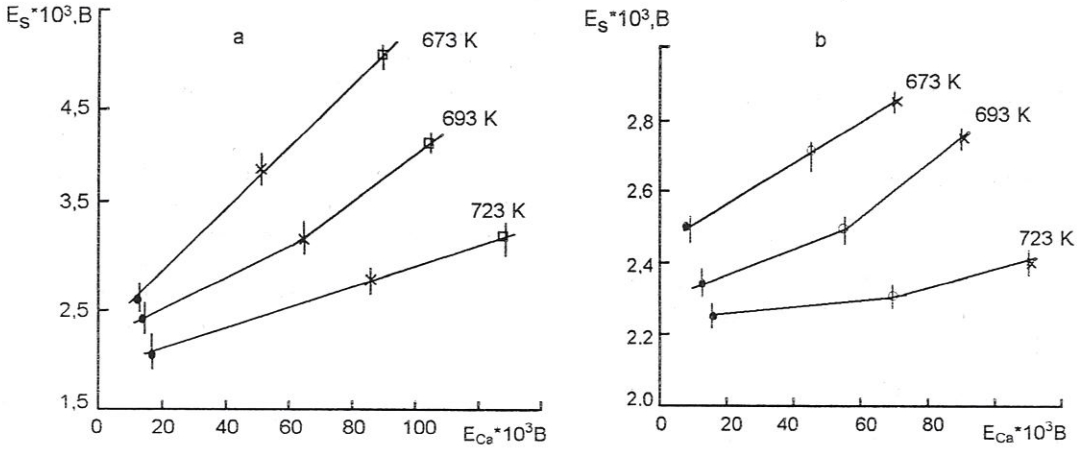

Fig. 1. Isothermal dependences $E_S = f(E_{Ca})$ for solid electrolytes (SEL): a — $CaSm_2S_4$ — x mole % CaS (x = • — 2, × — 8, □ — 10); b — $CaSm_2S_4$ — x mole % Sm_2S_3 (x = • — 2, □ — 4, × — 8).

$$\frac{dE_M}{d\mu_{Ln_2S_3}} = \frac{\tau_M}{q_M}, \qquad (13)$$

$$\frac{dE_S}{d\mu_{Ln_2S_3}} = \frac{\tau_S}{q_S}. \qquad (14)$$

The combined solution of equations (7, 8, 13, 14) provides the determination of chemical potential of doping Ln_2S_3 in a solid solution:

$$\mu_{Ln_2S_3} = \mu^0_{Ln_2S_3} + q_S\left(E_N - E_M\right) \qquad (15)$$

and its activity

$$-\ln a = \frac{q_S F}{RT}\left(E_M - E_S\right), \qquad (16)$$

where q_S is the charge of sulfide ion taking into account $t_e \rightarrow 0$ and prevailing sulfide ion conductivity type.

The research in temperature dependence of EMF for chain (1) in the electrolytic temperature range for the $CaGd_2S_4$ formation reaction from CaS and Gd_2S_3 made it possible to determine the changes in Gibbs' free energy, enthalpy and entropy calculated taking into account the temperature coefficient of EMF (Table 1). The process of $BaTm_2S_4$ formation from binary sulfides (BaS and Tm_2S_3) is exothermic and the exotherm is −284±2 kJ/mole.

The free energy of $CaGd_2S_4$ and $BaTm_2S_4$ formation from binary sulfides depends weakly on the temperature in the electrolytic range and tends to decrease with the temperature increase, thus, $CaGd_2S_4$ and $BaTm_2S_4$ are stable compounds in the temperature range 653 K to 723 K. Isothermal dependences $E_S = f(E_M)$ have been studied for a number of electrolyte systems from of various compositions. The curves for $CaS–Sm_2S_3$ system is shown in Fig. 1.

Transport numbers for M^{2+} and Ln^{3+} cations and for anions S^{2-} calculated using Equations (9–12) basing on experimental (dE_S/dE_M) values are presented in Table 2.

Table 2. Study results of electrolytic properties and non-stoichiometry of phases based on chalcolanthanates of alkali-earth metals

System	Phases based on MLn_2S_4	Region of solid solutions, mole%		σ_{gen}, Sm·cm^{-1}	t_M^{z+} ±0.01	t_S^{2-} ±0.01
		MS	Ln_2S_3			
$CaS–Sm_2S_3$	$CaS(\rightarrow CaSm_2S_4)$	10	20	10^{-6}–10^{-4}	0.01–0.02	1.00
	$Sm_2S_3(\rightarrow CaSm_2S_4)$				0.01 (0.05*)	1.00 (0.95*)
$CaS–Pr_2S_3$	$CaS(\rightarrow CaPr_2S_4)$	8	10	10^{-7}–10^{-5}	0.01–0.02	1.00
	$Pr_2S_3(\rightarrow CaPr_2S_4)$				0.00 –0.01	1.00
$BaS–Sm_2S_3$	$BaS(\rightarrow BaSm_2S_4)$	10	10	10^{-6}–10–4	–	–
	$Sm_2S_3(\rightarrow BaSm_2S_4)$				–	–
$CaS–Nd_2S_3$	$Nd_2S_3(\rightarrow CaNd_2S_4)$	–	20	10^{-7}–10^{-6}	0.00–0.08	0.92–1.00
$BaS–Nd_2S_3$	$Nd_2S_3(\rightarrow BaNd_2S_4)$	–	30	10^{-6}–10^{-5}	–	–
$CaS–Y_2S_3$	$CaS(\rightarrow CaY_2S_4)$	10	20	10^{-4}–10^{-3}	0.05–0.05*	0.95*–1.00
	$Y_2S_3(\rightarrow CaY_2S_4)$				0.03–0.01	0.92–1.00
$BaS–Tm_2S_3$	$BaS(\rightarrow BaTm_2S_4)$	16	30	10^{-3}–10^{-2}	0.02–0.03	1.00
	$Tm_2S_3(\rightarrow BaTm_2S_4)$				0.01–0.03	0.97
$CaS–Gd_2S_3$	$CaS(\rightarrow CaGd_2S_4)$	2	20	10^{-8}–10^{-6}	–	–
	$Gd_2S_3(\rightarrow CaGd_2S_4)$				0.00–0.06	0.94–1.00

* — data obtained by method of Tubandt.

The transfer numbers of cations are insignificant (0.00 to 0.05), whereas those of sulfide ions are close to unity (0.95 to 1.00) in all systems investigated by this method. The data obtained according to Tubandt [1, 6] agree well enough with those obtained in this work using the Chebotin-Obrosov method. The high transfer numbers for sulfide ions are most likely to be connected with the fact that the dimensions of the migration channel for sulfide ions (R_s = 0.911) in cubic lattice of the Th_3P_4 type satisfy the condition of sulfide ion transfer. At the same time, the size of channels calculated for M^{z+} migration (R_M= 0.498) are smaller than the range $0.54<R_k<0.62$ favorable from the viewpoint of space and energy for the M^{z+} ion transfer. That is why, in spite of the principal possibility of bipolar transfer, the major carriers are sulfide ions.

The activity of binary sulfides in ternary MLn_2S_4 has been calculated for all studied systems of various compositions using the equation (16). Figs. 2, 3 present the isotherms of $(-lg\, a_{M_xS_y(Ms)})$ and lgσ dependences on the solid electrolyte composition in $CaS–Y_2S_3$, $BaS–Tm_2S_3$, $CaS–Pr_2S_3$ and $CaS–Sm_2S_3$ systems. The content of binary sulfides in stoichiometric ternary compounds has been chosen as a standard state.

As it is seen from the figures, the activities of binary sulfides decrease with increasing content thereof in ternary MLn_2S_4. This phenomenon is probably connected with formation of neutral and charged associates of defects with opposite charges of the $/V''_M\ V^{\bullet\bullet}_S/$ or $/V''_{Ln}\ V^{\bullet\bullet}_S/$ type when the concentration thereof increases. A dependence of this kind does not contradict the phenomenological theory which considers the behavior of solid electrolytes to be similar to that of dilute solutions of strong electrolytes according to the Debye-Hueckel theory [14].

Comparing the dependence of binary sulfides activity to electric conductivity on the amount of alloying additive, it is possible to estimate reliably enough the phase stability limits based on the ternary compounds studied (Table 2). Temperature dependence of binary sulfide activity provides the calculation of the partial mole enthalpies of the solution thereof in ternary MLn_2S_4 using the relationship $\Delta\overline{H}_i = f(\partial \lg a_i / \partial T^{-1})$. As solid solutions of lanthanide sesquisulfides based on MLn_2S_4, in contrast to the alkali-earth metal sulfides, are inherent in all solid electrolytes studied in this work, we have considered the character of $\Delta\overline{H}_{iLn_2S_3}$

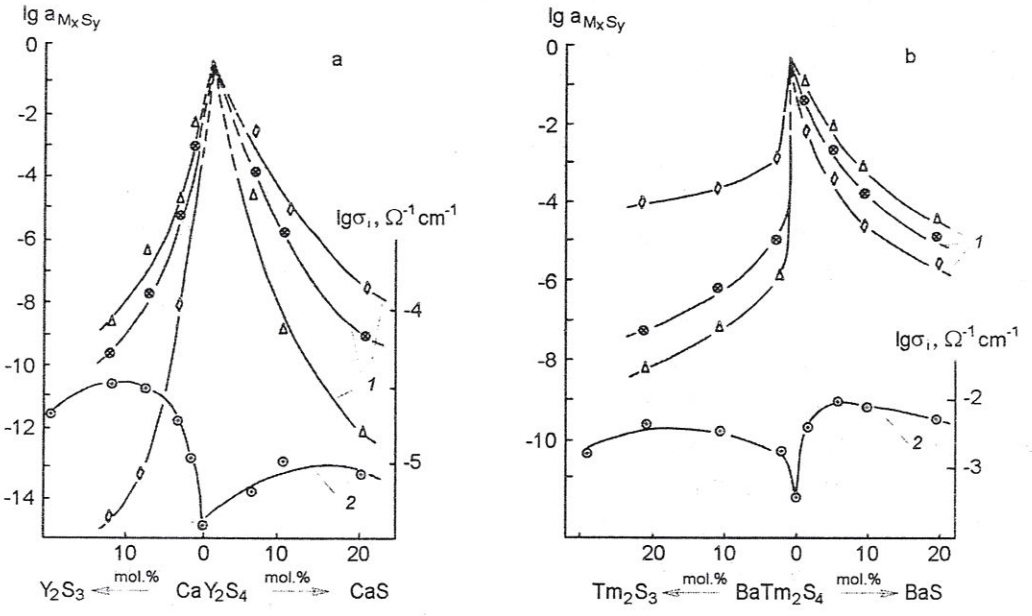

Fig. 2. Dependence of $lg\ a_{M_xS_y}$ (*1*) and lgσ (*2*) on composition of SEL: a — CaY_2S_4 — *x* mole % CaS (Y_2S_3); b — $BaTm_2S_4$ — *x* mole % BaS (Tm_2S_3).

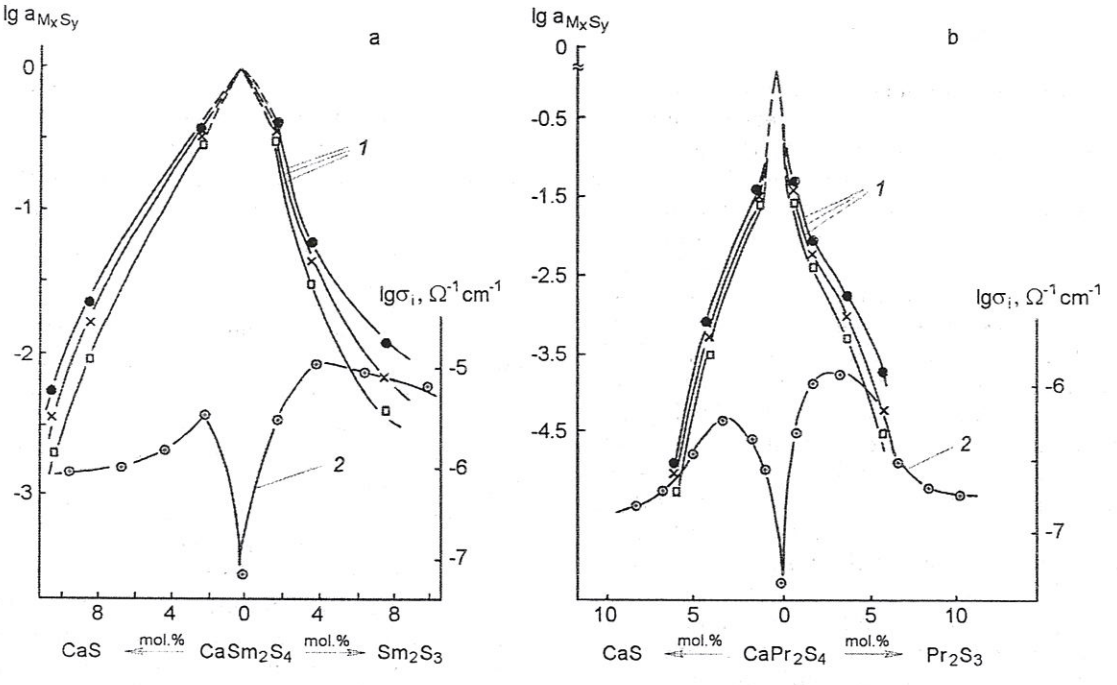

Fig. 3. Dependence of $lg\ a_{M_xS_y}$ (*1*) and lgσ (*2*) on composition of SEL: a — $CaSm_2S_4$ — *x* mol. % CaS (Sm_2S_3); b — $CaPr_2S_4$ — *x* mol. % BaS (Pr_2S_3).

variation as a function of sulfide solved (Fig. 4). The partial mole enthalpy of solution ($\Delta\overline{H}_i$) is obtained from ($\Delta\overline{H}$) values characterizing the dissociation, ionization, defect formation, annihilation, and associate formation processes. The defect formation enthalpy is a positive value, whereas the contribution of all other constituents depend insignificantly on the non-stoichiometry. According to Tretyakov [15,

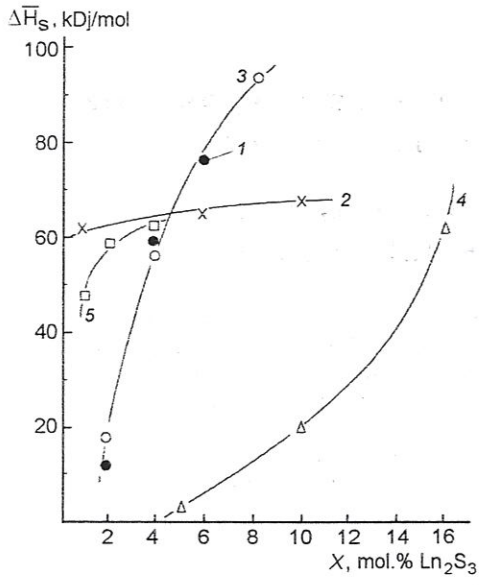

Fig. 4. Dependence of partial molar enthalpy of dissolution on concentration of doping component Ln_2S_3: *1* – CaY_2S_4, *2* – $BaTmS_4$, *3* – $CaSm_2S_4$, *4* – $CaNd_2S_4$, *5* – $CaPr_2S_4$.

16], the variation trend of the partial molar enthalpy of dissolution allows to judge the nature of defect formation mechanism: the $\Delta\overline{H}_i$ increase ($-\Delta\overline{H}_i$ reduction) during the alloying additive concentration growth (increase in non-stoichiometry) is connected with the increasing contribution of the vacancy formation.

The $\Delta\overline{H}_{Ln_2S_3}$ increase with the increasing x (Ln_2S_3 content) observed for all systems studied within the region of homogeneity is an additional confirmation to the vacancy mechanism of defect formation in solid electrolytes based on MLn_2S_4 which can be presented as:

$$Ln_2S_3(\rightarrow MLn_2S_4 \Longleftrightarrow 2Ln^{*}_{Ln} + 3\{S^{*}_{S}\} + V''_M + V^{\bullet\bullet}_S. \quad (17)$$

Thus, the use of electrochemical methods in the study of formation thermodynamics of ternary thiolanthanates of alkali-earth metals and phases based on those has allowed to consider $CaGd_2S_4$ and $BaTm_2S_4$ as stable compounds in the electrolytic temperature range 653–723 K; to find the stability limits for phases based on CaY_2S_4, $BaTm_2S_4$, $CaPr_2S_4$, $CaSm_2S_4$; to suggest a vacancy mechanism of defect formation in the doping process of these ternary compounds with binary sulfides.

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Термодинамічні характеристики тернарних сульфідів MLn_2S_4 та твердих розчинів на їх основі

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Методом ЕДС у різних модифікаціях виявлено термодинамічні характеристики тернарних сульфідів MLn_2S_4 і твердих розчинів на їх основі. Проведені дослідження дозволили вважати тверді електроліти $CaGd_2S_4$ і $BaTm_2S_4$ стійкими сполуками в електролітичному інтервалі 653–723 К. Одночасне виявлення активності бінарних сульфідів в тернарних $BaTm_2S_4$, CaY_2S_4, $CaSm_2S_4$, $CaPr_2S_4$, а також катіонних і аніонних чисел переносу зробило можливим оцінити межі стійкості фаз, запропонувати вакансійний механізм дефектоутворення і переважно сульфід-іонний тип провідності у твердих електролітах, що досліджувалися.