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Dependence of electrolytic properties of $CaYb_2S_4$ phases on the over-stoichiometric content of binary sulfides

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The $CaYb_2S_4$ phases with the over-stoichiometric content of CaS and Yb_2S_3 have been studied. The range of solid solutions, the temperature electrolytic interval, the average ion, cationic, anionic and electronic transfer numbers have been determined. The density values obtained by bottle method and by radiography are compared. The data obtained allow to consider the CaS solid solutions in calcium sulfoytterbiate as mixed ion conductors with a substantial contribution from electronic conductivity, while the phases with the over-stoichiometric Yb_2S_3 content, as sulfide-ionic solid electrolytes with the vacancy defect formation mechanism.

Исследованы фазы на основе $CaYb_2S_4$ со сверхстехиометрическим содержанием CaS и Yb_2S_3. Определена область твердых растворов, температурный электролитический интервал, средние ионные, катионные, анионные и электронные числа переноса. Сопоставлены пикнометрическая и рентгенографическая плотности. Полученные данные позволяют считать твердые растворы CaS в тиоиттербиате кальция смешанными ионными проводниками с существенным вкладом электронной проводимости, а фазы со сверхстехиометрическим содержанием Yb_2S_3 сульфид-ионными твердыми электролитами с вакансионным механизмом дефектообразования.

In the modern materials technology, the binary and ternary chalcogenides of high-melting (mainly rare) metals are of a great interest [1, 2]. The defect phases of general formula $MeLn_2S_4$ (Me = Ca, Ba; Ln = La, Y, Tm, Nd, Sm) crystallized in lattices such as $CaFe_2O_4$ and Th_3P_4, have been shown to be solid electrolytes (SE) with predominant sulfide-ion conduction. The appearance of sulfide-ion conductivity in those compounds is combined with formation of double-ionized vacancies in the sulfur sublattice as a result of alloying ternary sulfides with binary ones.

Defect phases on the basis of calcium thioytterbiate are crystallized in an orthorhombic lattice of the Yb_3S_4 type where ions Yb^{2+} are displaced by Ca^{2+} ones. The only known sulfide-conductive solid electrolyte of the same structural type is CaY_2S_4 [3]. This work makes it possible to extent the field of the known sulfide-conductive solid electrolytes. In the work frame, the synthesis and annealing techniques have been developed for $CaYb_2S_4$ ternary compound and phases on its basis as well the samples obtained have been identified. To determine the defect formation character, the bottle density was compared to the radiographic one calculated assuming the vacancy and interstitial mechanism of defect formation. The temperature electrolytic interval and extension of defect phases on the ternary $CaYb_2S_4$ basis were studied under account for dependence of electric conductivity on the temperature and phase structure. To elucidate the effect of electron transfer on the electrolytic properties of obtained

$CaYb_2S_4$ phases, electron and average ion transfer numbers were measured. The subdivision of the ion conductivity component into cationic and anionic ones has confirmed the existence of sulfide transfer in the phases with over-stoichiometric Yb_2S_3 content.

The sulfide material was synthesized by a ceramic method. The analytical purity grade calcium oxide and ytterbium (III) oxide were used as initial materials. The dried and pulverized mixtures in a graphite boat were loaded into the reactor, heated to 1073 K in argon flow; then, the reactor was fed with argon and carbon disulfide (volume flow of the sulfidizing mixture 0.6–0.7 dm^3/h). Thus temperature was increased up to 1273 K and hold during 8 hours, then the charge was cooled in argon flow. To obtain more dense samples, the synthesized powders were compacted into tablets and exposed to homogenizing annealing in a flow of argon with carbon disulfide (to suppress desulfidation) for 10 hours at 1293–1323 K. The sulfidation completeness was controlled by the iodometric method. The chemical analysis results of the sample synthesized have confirmed that the selected method and the mode of synthesis provide complete sulfidation of the initial oxides.

The X-ray phase examination of samples was carried out using a DRON-3M diffractometer ($CuK\alpha$ emission) at the scanning step 0.1°, exposure time 2 s, the scanning range 20°–60°. Silicon was used as an internal standard for calculating the unit cell parameters. The complex electric conductivity of all the synthesized samples was measured by the two-electrode method with graphite electrodes using a digital measuring instrument E-7-20 within the range of room temperature up to 773 K at 10 kHz frequency. The error was 10 % of the nominal measured value.

The average ion transfer numbers ($\bar{t}_i$) were measured in a galvanic cell with the electrodes reversible relatively to sulfide-ions:

$$C|Fe|FeS|CaYb_2S_4 - Yb_2S_3(CaS)|Cu_2S|Cu|C \quad (1)$$

and determined from the ratio of the measured and theoretical EMF calculated under condition of use in the cell (1) hypothetical SE with only ion conductivity.

The electron transfer numbers (t_e) were determined using polarization method [4] in an electrochemical cell:

$$(-)C|Fe|FeS|CaYb_2S_4 - Yb_2S_3(CaS)|C(+) \quad (2)$$

in the voltage range 0.1–2 V. The electronic conductivity was calculated as:

$$\sigma_{el} = \frac{z \cdot F \cdot l}{R \cdot T \cdot S} \cdot I, \quad (3)$$

where I is the saturation electron current; z, ion charge; F, the Faraday number; R, universal gas constant; l and S — geometric parameters of the solid electrolyte. The electron transfer numbers were determined taking in to account the complex electric conductivity.

The ion component of conductivity was subdivided into cationic and anionic ones using the Chebotin-Obrosov method [5] in concentration cells with transfer, reversible relative to sulfide-ion and calcium ion:

$$C|Fe|FeS|CaYb_2S_4|CaYb_2S_4 - x \text{ mol.\% } Yb_2S_3|FeS|Fe|C, \quad (4)$$

$$C|Ca|CaYb_2S_4 - x \text{ mol.\% } Yb_2S_3|CaYb_2S_4|Ca|C. \quad (5)$$

Due to high activity of calcium electrodes, the experiments were conducted using the instantaneous tangency method [6]. The diffusion potential in both cells arises at the interface of the stoichiometric compound and solid solutions of binary sulfides on its basis. The EMF of the element (5) reversible relative to calcium ions (E_{Ca}) is connected with transfer numbers of sulfur and ytterbium ions. The EMF of the element (4) reversible relative to sulfide ions (E_S) is connected with transfer numbers of calcium and ytterbium. Provided the data statistics is large enough, the method allows to define transfer numbers of ions at an accuracy of ±0.02. The major carrier ion type was determined under account for isothermal relations $E_S = f(E_{Ca})$ for electrolytes of different structure using equations:

$$t_{S^{2-}} = \tau_{Ca} \quad (6)$$

$$-\tau_S = t_{Ca^{2+}}, \quad (7)$$

where τ_S is the concentration changes in the cell (4); τ_{Ca}, those in the cell (5); $t_{S^{2-}}$, transfer numbers of sulfide ions; $t_{Ca^{2+}}$, those of calcium ions.

The bottle density was determined in accordance with International Standard ISO 5018-83.

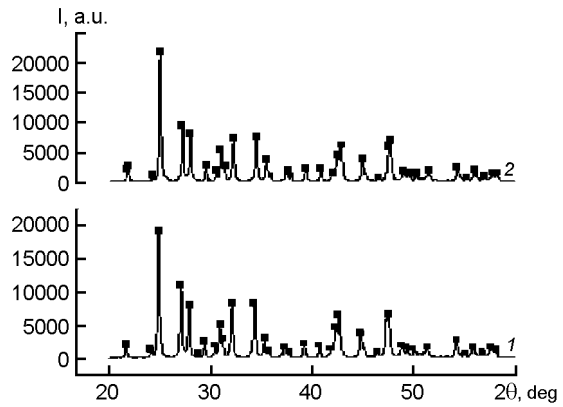

Fig. 1. XRD patterns for $CaYb_2S_4$ (*1*) and $CaYb_2S_4$ – 2 mol. % Yb_2S_3 (*2*).

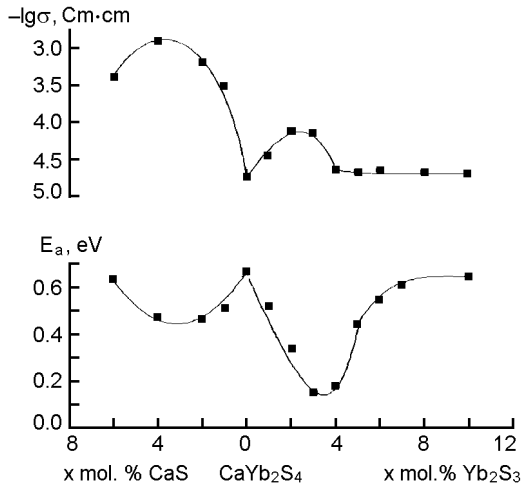

Fig. 2. Dependences of electric conductivity logarithm and activation energy on solid electrolyte composition of $CaYb_2S_4$–x mol.% Yb_2S_3 (CaS) system at 673 K.

Using ceramic technology, the stoichiometric compound $CaYb_2S_4$ and samples with over-stoichiometric content of binary sulfides CaS and Yb_2S_3 were synthesized. The X-ray phase analysis (XPA) of the samples in the range $(100-x)$CaS–$x$$Yb_2S_3$, where $x = 47$ to 55 mol.% Yb_2S_3, has shown the presence of a single phase $CaYb_2S_4$ which is crystallized in orthorhombic structure of the Yb_3S_4 type. The X-ray diffraction (XRD) patterns of synthesized samples where $x < 0.47$ and $x > 0.55$ mole fraction of Yb_2S_3 contained reflections from the second phase, calcium sulfide and ytterbium sulfide, respectively. The XRD patterns for samples of stoichiometric structure and for those containing an excess 2 mol.% of Yb_2S_3 are shown in Fig. 1. Thus, the synthesized samples can be presented as phases $CaYb_2S_4$–$x$$Yb_2S_3$ and $CaYb_2S_4$–yCaS (where x varies from 0 to 10 mol. % Yb_2S_3 and y from 0 to 6 mol. % CaS) and the general chemical formulas for solid solutions of the highest concentration can be presented as $CaYb_{1.88}S_{3.82}$ and $Ca_{0.9}Yb_2S_{3.9}$.

The temperature dependence of complex electric conductivity was studied in the 298–833 K range. The selection of the upper temperature limit is conditioned by a possibility of changes in the sample structure due to sulfur loss resulting from thermal dissociation at the further temperature rise. For samples of all structures in the investigated system, the relationships $lg\sigma = f(10^3/T)$ have shown a change in the curve slope at 470–550 K in the samples with CaS excess in $CaYb_2S_4$, and at 470–590 K in the samples with Yb_2S_3 excess in $CaYb_2S_4$. The temperature coefficient of electric conductivity in the high-temperature segment of curves varies from 0.15 to 0.67 eV, which corresponds mainly to ion conductivity.

Electric conductivity in phases with excess calcium sulfide in $CaYb_2S_4$ is higher by 1–1.5 decimal orders than in phases with excess Yb_2S_3, which can be explained by an increased contribution from the electronic constituent into conductivity at calcium sulfide alloying of $CaYb_2S_4$ due to incomplete ionization of vacancies in the ytterbium sublattice, since ytterbium is polyvalent and changes its oxidation states easily.

From the conductometric data, dependences were constructed for isotherm of electric conductivity logarithm and isotherm of activation energy on the system composition of at 673 K (Fig. 2). The shown $lg\sigma$ and E_a dependences near stoichiometric $CaYb_2S_4$ are well described from the viewpoint of vacancy defect formation mechanism in the case of formation of two-sided range of solid solutions and allow to evaluate the solid solution field boundaries for over-stoichiometric content CaS and Yb_2S_3 which agree well with XPA data.

The electronic transfer numbers were measured by the Hebb-Wagner method in the electrochemical cell (2) with one blocking electrode and one electrode reversible relative to sulfide ion at temperatures 603, 643, and 673 K. The samples with the over-stoichiometric calcium sulfide content as well a those alloyed with ytterbium sulfide were studied. The current-voltage characteristics (IVC) for solid solutions of CaS in

Table 1. Average ion and electronic transfer numbers for $CaYb_2S_4$ – x mol.% Yb_2S_3 system

Composition, $CaYb_2S_4$ – x mol.% Yb_2S_3	603 K		643 K		673 K	
	$\bar{t}_i \pm 0.05$	$t_e \cdot 10^2$	$\bar{t}_i \pm 0.05$	$t_e \cdot 10^2$	$\bar{t}_i \pm 0.05$	$t_e \cdot 10^2$
0	0.82	1.92	0.79	1.80	0.75	2.33
2	0.93	0.57	0.86	0.61	0.81	0.69
4	0.97	0.38	0.94	0.36	0.89	0.33
6	0.89	1.12	0.86	1.01	0.83	1.01
8	0.88	1.45	0.85	1.75	0.82	1.43
10	0.85	–	0.82	1.50	0.81	1.68
12	0.84	1.24	0.82	1.40	0.77	1.52

$CaYb_2S_4$ had no plateaus corresponding to the saturation current. As the Hebb-Wagner method is used to determine the electron transfer numbers in mixed conductors with predominant ion conductivity ($\bar{t}_i \geq 0.9$) [7], the absence of results at the usage of that technique confirms the conclusion on a considerable contribution from electron conductivity for the phase with over-stoichiometric content of CaS made basing on conductometric research.

The general view of IVCs obtained at electron transfer numbers determination at 673, 693, and 713 K is the same both for stoichiometric $CaYb_2S_4$ and samples with excess ytterbium sulfide. The electron saturation current increases regularly as the temperature rises. This can be explained by the ability of the studied sulfides to lose sulfur easily at a high temperature due to thermal dissociation that may cause a deviation from stoichiometry towards excess of metal and to appearance of electronic conductivity resulting from the metal ionization accompanied by transition of electrons into conduction zone. The electron transfer numbers were calculated from the data on electron saturation current (Table 1). The fraction of electron transfer in phases with over-stoichiometric Yb_2S_3 content is insignificant ($t_e \sim 10^{-2}$). However, it is to note that use of graphite as the blocking electrode results in overestimated electron transfer numbers. Therefore, the electrolytic properties of investigated solid electrolytes are better and the true contribution from electron (not hole) conductivity is lower than it follows from the data obtained using the Hebb-Wagner method ($t_e \leq 10^{-2}$) [8].

The study of electric conductivity and electron transfer numbers has shown that solid solutions on the basis of calcium thioytterbiate alloyed with calcium sulfide

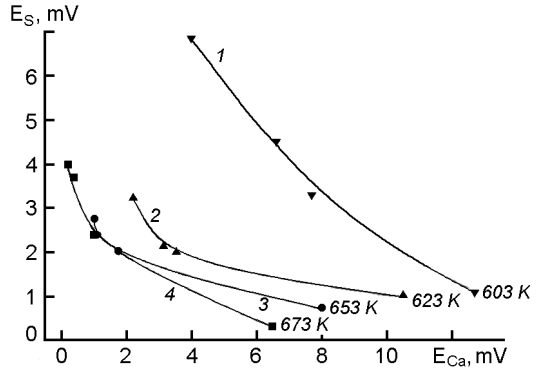

Fig. 3. Isothermal dependences $E_S = f(E_{Ca})$ for the solid electrolyte $CaYb_2S_4$ — x mol.% Yb_2S_3: $CaYb_2S_4$ — 1 mol.% Yb_2S_3 (*1*); $CaYb_2S_4$ — 2 mol.% Yb_2S_3 (*2*); $CaYb_2S_4$ — 6 mol.% Yb_2S_3 (*3*); $CaYb_2S_4$ — 10 mol.% Yb_2S_3 (*4*).

are mixed ion conductors with a substantial contribution from electron conductivity. Therefore, the electrolytic properties were studied only for phases on the basis of $CaYb_2S_4$ with the over-stoichiometric ytterbium sulfide content.

The average ion transfer numbers obtained by the EMF method depend weakly on composition and temperature, however, increase somewhat at the temperature of 603 K close to lower limit of the electrolytic temperature interval (Table 1). This may be connected to reduction of thermal dissociation accompanied by the appearance of mobile electrons at temperature dropping. From the data of Table 1, it can be concluded that stoichiometric $CaYb_2S_4$ and solid solutions of Yb_2S_3 on its basis are conductors with predominant carriers of ion type.

The subdivision of the ion conductivity component into cationic and anionic ones was performed in concentration cells (4) and

Table 2. Cationic and anionic transfer numbers in the $CaYb_2S_4$–Yb_2S_3 system

Composition, x mol. % Yb_2S_3	Temperature, K							
	673		653		623		603	
	t_S^{2-}±0.02	t_{Ca}^{2+}±0.02	t_S^{2-}±0.02	t_{Ca}^{2+}±0.02	t_S^{2-}±0.02	t_{Ca}^{2+}±0.02	t_S^{2-}±0.02	t_{Ca}^{2+}±0.02
1	1.02	0.02	1.01	0.01	1.01	0.01	1.01	0.01
2	1.02	0.02	1.01	0.01	1.01	0.01	1.01	0.01
6	1.01	0.01	1.01	0.01	1.00	0.00	1.01	0.01
10	1.00	0.00	1.00	0.00	1.00	0.00	1.00	0.00

(5) [9]. Isothermal dependences $E_S = f(E_{Ca})$ for electrolytes of various compositions are presented in Fig. 3. The transfer numbers for calcium and sulfur ions calculated from experimentally obtained (dE_S/dE_{Ca}) values are listed in Table 2. The transfer numbers for calcium ions are within the method error. It can be stated at a high probability that the studied samples of solid solutions on the basis of calcium thioytterbiate with over-stoichiometric Yb_2S_3 content in the temperature range of 603–673 K are practically unipolar sulfide conductive solid electrolytes.

Formation of solid solutions of binary sulfides on the basis of $CaYb_2S_4$ may follow two main structure models:

(1) substitution by impurity cations and anions of their intrinsic positions in the ternary compound lattice with vacancies formation in sublattices of sulfur and of the second cation (vacancy mechanism of disordering):

$$CaS(\rightarrow CaYb_2S_4) \rightleftarrows \rightleftarrows Ca_{Ca}^{*} + S_S^{*} + 2V_{Yb}^{'''} + 3V_S^{\bullet\bullet}, \quad (8)$$

$$Yb_2S_3(\rightarrow CaYb_2S_4) \rightleftarrows \rightleftarrows 2Yb_{Yb}^{*} + 3S_S^{*} + V_{Ca}^{''} + V_S^{\bullet\bullet}. \quad (9)$$

However, as its follows from conductometric research and from multivalency of ytterbium, the defect formation in the case of ternary compound alloying with calcium sulfide may result in an incomplete ionization of the ytterbium vacancies and appearance of mobile electrons in the conductivity zone:

$$CaS(\rightarrow CaYb_2S_4) \rightleftarrows \rightleftarrows Ca_{Ca}^{*} + S_S^{*} + 2Va_{Yb}^{''} + 3V_S^{\bullet\bullet} + 2\bar{e}. \quad (10)$$

(2) introduction of the impurity cation and anion in interstice of $CaYb_2S_4$ lattice with formation of balanced interstitial defects (interstitial mechanism of disordering):

$$CaS(\rightarrow CaYb_2S_4) \rightleftarrows \rightleftarrows Ca_i^{\bullet\bullet} + S_i^{''} + Ca_{Ca}^{*} + 2Yb_{Yb}^{*} + 4S_S^{*}, \quad (11)$$

$$Yb_2S_3(\rightarrow CaYb_2S_4) \rightleftarrows \rightleftarrows 2Yb_i^{\bullet\bullet} + 3S_i^{''} + Ca_{Ca}^{*} + 2Yb_{Yb}^{*} + 4S_S^{*}. \quad (12)$$

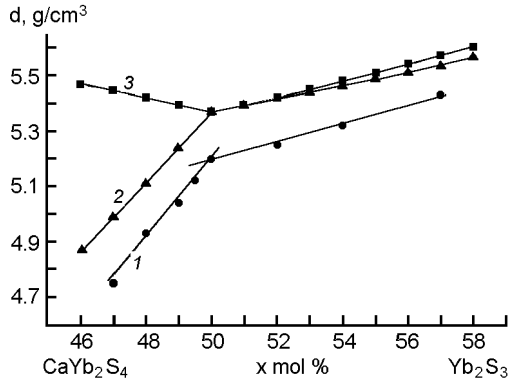

Fig. 4. Dependence of density on the solid electrolyte composition in the (100–x)CaS – $x$$Yb_2S_3$ system: bottle density (*1*); X-ray density calculated basing on vacancy mechanism (*2*) and interstitial mechanism (*3*).

To elucidate the possible defect formation character, we measured the bottle density of stoichiometric calcium thioytterbiate and that of the samples alloyed with calcium and ytterbium sulfides in quantities corresponding to the area of solid solutions determined before. Moreover, for hypothetical vacancy and interstitial disordering models, the radiographic (theoretical) density of solid phases under study was calculated. The dependence of the experimental (bottle) and radiographic density calculated for different defect formation models on the composition of binary sulfide solid solutions in $CaYb_2S_4$ is presented in Fig. 4. The character of the bottle density dependence on composition is described well enough within

the vacancy disordering mechanism. Perhaps formation of solid solutions on the basis of ternary $CaYb_2S_4$ in the system under study is accompanied by formation of ionized vacancies according to equations (9), (10). Moreover, the research has shown that the synthesized samples show good ceramic properties, as their experimental density is 95–98 % of the theoretical one.

The dependences of average ion, electronic transfer numbers and electric conductivity on the composition is shown in Fig. 5. The stoichiometric $CaYb_2S_4$ is seen to be characterized by minimum average ion transfer numbers and maximum average electron ones, that is connected with a low concentration of the ion defects originating only due to intrinsic disordering. Therefore, the fraction of electron conductivity originating sue to the sulfur exchange between the solid electrolyte and the gas phase (13) increases.

$$CaYb_2S_4 \rightleftarrows \quad (13)$$
$$\rightleftarrows Ca^*_{Ca} + 2Yb^*_{Yb} + 3S^*_S + \frac{1}{2}S_2\uparrow + V^{\bullet\bullet}_S + 2\bar{e},$$

At introduction of 1 to 4 mol.% Yb_2S_3 as an alloying impurity, the electric conductivity and ion transfer numbers increase but electronic transfer numbers drop, because, according to (10), the concentration of ion defects increases. Obviously, for these structures, ionized vacancies of sulfur and metal atoms are most likely in amounts answering to the "dilute solution" concept [10]. The vacancy mobility values in such a solution are maximum. However, a further increase concentration of alloying Yb_2S_3 to 6–8 mol.% results in reduction of contribution from ion transfer and increase of that from electron one, most likely due to formation of oppositely charged defects associates $/V^{\bullet\bullet}_S \cdot V''_{Ca}/$. The constant values of average ion and electron transfer numbers for samples containing more than 8 mol.% of ytterbium sulfide allow to suggest the attainment of the solid solution region boundary and transition to a two-phase system.

To conclude, the study has allowed to confirm the existence and determine the extension of CaS,Yb_2S_3 solid solutions area on the basis of $CaYb_2S_4$ (ST Yb_2S_4); to consider phases with the over-stoichiometric calcium sulfide content as mixed ion conductors with substantial contribution from electron conductivity; to consider the sulfidic ceramics with the over-stoichiometric ytterbium sulfide content as solid electrolytes with predominant ion conductivity. The defect structure of phases on the basis of $CaYb_2S_4$ is identified as a vacancy one.

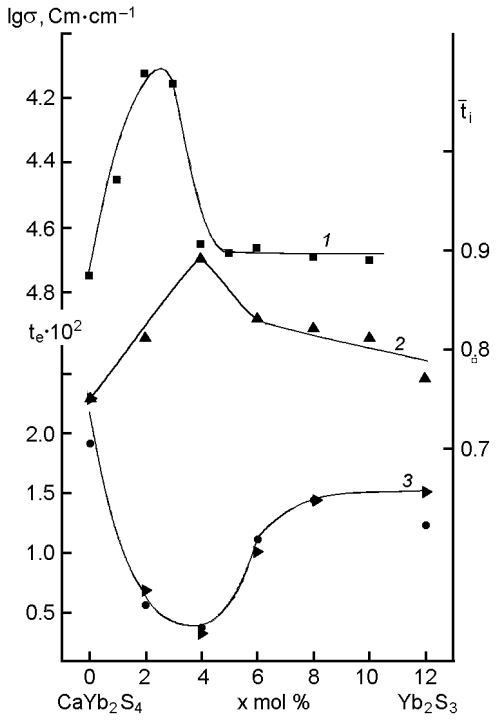

Fig. 5. Composition-property dependences for $CaYb_2S_4$ – x mol. % Yb_2S_3 system: electric conductivity (*1*); average ion transfer numbers (*2*); electron transfer numbers (*3*).

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References

1. L.A.Kalinina, G.I.Shirokova, I.V.Murin, Ju.N.Ushakova, *J.Appl.Chem.*, **73**, 1324 (2000).
2. L.A.Kalinina, Ju.N.Ushakova, H.G.Fominykh, O.V.Medvedeva, *Curr.Appl.Phys.*, doi:10.1016/j.cap.2007.04.013 (2007).
3. L.A.Kalinina, G.I.Shirokova, M.V.Ljalina, in: Trans. of UC, Russian Academy of Sciences: Electrodics of Solid State Systems, Sverdlovsk (1991), p.18.
4. R.V.Gusejnov, F.I.Kukoz, Electronic Processes in Solid Electrolytes, Rostov na Donu Univ. (1986) [in Russian].
5. N.V.Chebotin, V.P.Obrosov, in: Papers of Inst. Electrochemistry UFAS USSR, v.18, Sverdlovsk (1972), p.151.
6. Ya.I.Gerasimov, I.V.Kutsenok, V.A.Geiderikh, *Dokl.AN USSR*, **44**, 633 (1979).
7. Ju.Ya. Gurevitch, Solid Electrolytes, Nauka, Moscow (1986) [in Russian].
8. O.V.Medvedeva, L.A.Kalinina, Ju.N.Ushakova, *Functional Materials*, **13**, 321 (2006).

9. L.A. Kalinina, Ju.N. Ushakova, O.V. Medvedeva, *Zh. Fiz. Khim.*, **80**, 1731 (2006).

10. V.N.Chebotin , M.V.Perfil'ev, Electrochemistry of Solid Electrolytes, Khimiya, Moscow (1978) [in Russian].

Залежність електролітичних та керамічних властивостей фаз на основі $CaYb_2S_4$ від надстехіометричного вмісту бінарних сульфідів

Л.О.Калініна, Ю.М.Ушакова, Б.О.Ананченко, О.Г.Фоміних, Г.І.Широкова

Досліджені фази на основі $CaYb_2S_4$ з надстехіометричним вмістом CaS та Yb_2S_3. Визначено область твердих розчинів, температурний електролітичний інтервал, середні іонні, катіонні, аніонні та електронні числа переносу. Порівняно пікнометричну та рентгенографічну густину. Одержані дані дозволяють вважати тверді розчини CaS у тіоіттербіаті кальцію змішаними іонними провідниками з вагомим вкладом електронної провідності, а фази з надстехіометричним вмістом Yb_2S_3 — сульфід-іонними твердими електролітами з вакансійним механізмом дефектоутворення.