Conductive properties of solid solutions of the system xYF$_3$–(1–x)BaF$_2$–SnF$_2$

R.M.Pshenychnyi[1], **O.V.Lysenko**[2], **T.V.Pavlenko**[2], **A.O.Omelchuk**[2]

[1]Sumy State University, 2 Rymskogo-Korsakova St.,
40007 Sumy, Ukraine

[2]V.I.Vernadsky Institute of General and Inorganic Chemistry, National
Academy of Sciences of Ukraine, 32-34 Acad. Palladina Ave.,
03680 Kyiv, Ukraine

The article is devoted to the study of the effect of replacing Ba^{2+} ions with Y^{3+} in the BaSnF$_4$ structure on the conductive properties of Ba$_{1-x}$Y$_x$SnF$_{4+x}$ solid solutions obtained for the first time. The synthesis was carried out in 2 stages. First, solid solutions Ba$_{1-x}$Y$_x$SnF$_{2+x}$ (0.01 < x < 0.15) isostructural with BaF$_2$ (cubic modification) were synthesized by the coprecipitation method. At the next stage, solid solutions Ba$_{1-x}$Y$_x$SnF$_{4+x}$ (x = 0.03, 0.05, 0.10) isostructural with BaSnF$_4$ were prepared by the sintering process. It was established that an increase in the content of yttrium in the structure of the solid solution leads to an increase in conductivity and a decrease in the activation energy of ionic conductivity. It was found that the solid solution Ba$_{0.90}$Y$_{0.10}$SnF$_{4.10}$ (σ = 1.53·10^{-3} S/cm at 353 K) is characterized by the highest conductivity values among the obtained phases.

Keywords: fluoride-ion electrolytes, substitutional solid solutions, X-ray diffraction analysis (XRD), electrical conductivity, activation energy of ionic conduction, impedance spectroscopy.

Провідні властивості твердих розчинів системи xYF$_3$–(1–x)BaF$_2$–SnF$_2$.
Р.М.Пшеничний, О.В.Лисенко, Т.В.Павленко, А.О.Омельчук

Статтю присвячено дослідженню впливу заміщення іонів Ba^{2+} на Y^{3+} в структурі BaSnF$_4$ на провідні властивості твердих розчинів Ba$_{1-x}$Y$_x$SnF$_{4+x}$, що одержані вперше. Синтез здійснювали в 2 стадії. Спочатку методом сумісного осадження одержано тверді розчини Ba$_{1-x}$Y$_x$SnF$_{2+x}$ (0.01 < x < 0.15) ізоструктурні BaF$_2$ кубічної модифікації. На наступному етапі методом сплавлення одержано тверді розчини Ba$_{1-x}$Y$_x$SnF$_{4+x}$ (x = 0,03; 0,05; 0,10) ізоструктурні BaSnF$_4$. Встановлено, що збільшення вмісту ітрію в структурі твердого розчину призводить до збільшення провідності та зниження енергії активації іонної провідності. Виявлено, що найвищими показниками провідності серед отриманих фаз характеризується твердий розчин Ba$_{0.90}$Y$_{0.10}$SnF$_{4.10}$ (σ = 1.53·10^{-3} См/см при 353 K).

1. Introduction

In recent years, studies of new solid electrolytes with ionic conductivity have begun to develop rather actively. These materials are widely used in chemical current sources with a high specific capacity, supercapacitors, electrochemical sensors, ion-selective electrodes, etc. [1–3]. Solid electrolytes with fluoride-ion conductivity, based on barium and tin fluorides are promising materials that can be used in electrical devices for various functional purposes [4, 5]. These salts form stoichiometric compounds BaSnF$_4$, BaSn$_2$F$_6$ and solid solutions of the system (BaF$_2$)$_x$–(SnF$_2$)$_{1-x}$ [6]. A feature of SnF$_2$ is the presence of a stereoactive lone pair of electrons (5s^2) in Sn^{2+}, which significantly affects the distribution of fluorine anions and their mobility in the anionic sublattice [7].

$BaSnF_4$ crystallizes belong to the tetragonal syngony with a layered structure, in which layers BaBaSnSnBaBa... alternate parallel to the c axis of the unit cell [8]. Due to this arrangement of cations, mobile fluorine anions in the solid electrolyte structure are localized mainly between Ba–Sn and Sn–Sn. Fluorine anions localized between the Ba–Ba layers are practically immobile and are a kind of a barrier for conductivity in the polycrystalline material; therefore, the movement of fluorine ions occurs due to a jump into the space between Ba–Sn [9]. Therefore, the conductive properties of compounds of this type should substantially depend not only on defects in the crystal lattice, but also on their location in the anionic sublattice between cation layers.

To increase the disorder in the $BaSnF_4$ structure, barium ions are replaced by mono- and trivalent cations, resulting in the formation of anion-deficient and anion-excess solid solutions, which positively affects the conductive properties of the non-stoichiometric phases. The authors of [10, 11] showed that replacing Ba^{2+} with Nd^{3+} and Eu^{3+} up to 0.03–0.04 mol increases the conductivity of the formed solid solutions due to the formation of interstitial fluorine ions. A further increase in the content of the substituents leads to a decrease in the conductivity of the solid electrolyte.

In [6, 12, 13], the structure and conductive properties of solid solutions formed in the BaF_2–SnF_2 system were investigated. It was established that the change in the ratio between the starting substances affects the electrical conductivity of the formed phases. The $Ba_{0.47}Sn_{0.53}F_{4.00}$ solid solution is characterized by the highest electrical conductivity ($\sigma = 4.1 \cdot 10^{-3}$ S/cm at room temperature) and the lowest activation energy ($E_a = 17.9$ kJ/mol) of the ionic conductivity [6].

In order to find new solid electrolytes with fluoride ion conductivity that can be used in electrochemical devices of various functional purposes, the effect of replacing Ba^{2+} ions with Y^{3+} in the $BaSnF_4$ structure on the conductive properties of the formed solid electrolytes was investigated.

2. Experimental

To obtain solid solutions in the system xYF_3–$(1–x)BaF_2$–SnF_2, the following chemicals were used: $Ba(NO_3)_2$ (99.95 %), $Y(NO_3)_3 \cdot 6H_2O$ (99 %), SnF_2 (99 %) and NH_4F (99 %).

The solid solutions in the xYF_3–$(1–x)BaF_2$–SnF_2 system were synthesized in two stages [14]. At the first stage, solid solutions based on barium fluoride $Ba_{1–x}Y_xF_{2+x}$ ($x = 0.01$; 0.03; 0.05; 0.07; 0.10; 0.15) were obtained by co-precipitation. First, 0.1 M solutions of $Ba(NO_3)_2$ with $Y(NO_3)_3$ salts were prepared by mixing in the appropriate ratio and stirring for 10 minutes on a magnetic stirrer; then the resulting mixture was added dropwise to the NH_4F solution taken with a sevenfold excess for complete co-precipitation of yttrium and barium fluorides.

At the second stage, the resulting solid solutions were fused with SnF_2, taken in an amount calculated to form $Ba_{1–x}Y_xSnF_{4+x}$ solid solutions. The process was carried out at a temperature of 773–823 K for 30–60 min in an argon atmosphere to prevent the formation of oxides and oxofluorides. The higher the content of yttrium in the $Ba_{1–x}Y_xF_{2+x}$ solid solutions, the higher the temperature of the process and its duration necessary for the complete interaction of the components of the reaction mixture.

X-ray diffraction analysis (XRD) of the synthesized samples was performed on a DRON-3M diffractometer using CuK_α radiation in the range of angles from 10 to 80 deg with a step of 0.04 deg and an exposure of 3 s at each point. The JCPDS database was used to identify the diffraction patterns. The diffraction patterns were processed using the Match and UnitCell programs.

The chemical composition of $Ba_{1–x}Y_xSnF_{4+x}$ solid solutions was determined using an SEO-SEM Inspect S50-B scanning electron microscope equipped with an AZtecOne energy-dispersive X-ray spectrometer with an X-MaxN20 detector (Oxford Instruments plc.). The measurement error is up to 3 %.

The conductive properties of solid electrolytes were studied by the alternating current method in a two-electrode scheme using a P5083 alternating current bridge. Pressed cylindrical polycrystalline samples with a diameter of 8.0 mm and a thickness of 2.0–3.0 mm were used. The current leads to the samples were polished platinum plates.

The temperature dependence of the electrical conductivity of complex fluorides was studied at a frequency of 70 kHz. After thermostating the sample in the cooling mode, measurements were made in an argon environment in the range of 298 to 673 K. The temperature measurement error is up to 1 %, and the electrical conductivity is up to 4 %.
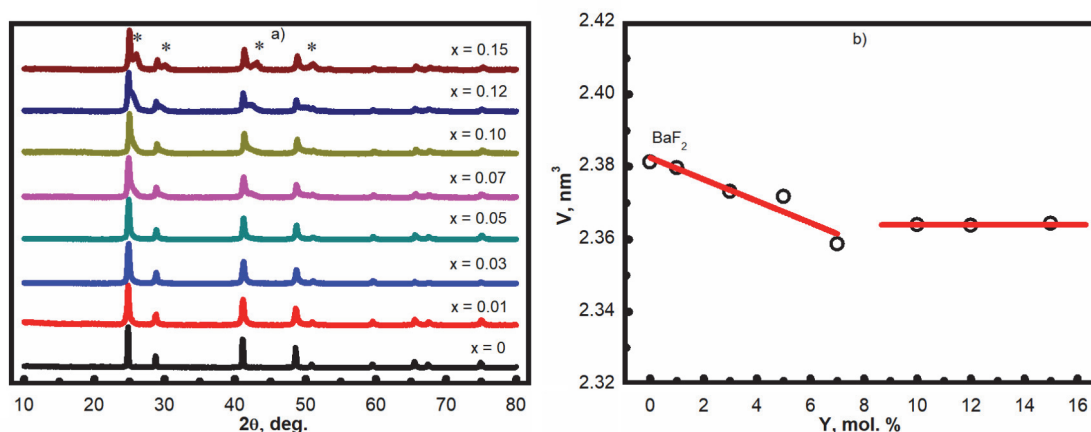
Fig. 1. Diffraction patterns (a) and unit cell volumes (b) of $Ba_{1-x}Y_xF_{2+x}$ solid solutions.

The specific electrical conductivity was calculated according to the equation:

$$\sigma = l/s \cdot R,$$

where l is the thickness of the cylindrical sample, s is the contact area, and R is the active resistance.

The impedance was measured with an E7-30 broadband dielectric spectrometer with an immitance meter (RLC). Pressed cylindrical polycrystalline samples 8.0 mm in diameter and 2.2 mm thick were placed between two polished platinum electrodes in a sample cuvette, which was then heated to operating temperature. After thermostating the sample in the cooling mode, measurements were performed in the range of 25 Hz to 3 MHz from room temperature to 473 K. The measurement error is up to 3 %. The electrochemical impedance spectrum of the solid electrolyte was simulated using the EIS Spectrum Analyzer software.

3. Results and discussion

The obtained solid solutions of the composition $Ba_{1-x}Y_xF_{2+x}$ have a cubic crystal lattice (space group $Fm3m$) and are isostructural with BaF_2 (JCPDS card No. 00-004-0452) (Fig. 1a). The volume of the unit cells of the synthesized fluorides monotonically decreases with an increase in the content of yttrium in the structure due to the replacement of a larger Ba^{2+} by smaller Y^{3+} ions. This change can be traced up to the yttrium content of 0.07 mol (Fig. 1b). The effective ionic radii of Ba^{2+} and Y^{3+} are 0.135 and 0.090 nm, respectively (for VI coordination) [15]. Unit cell volumes decrease from 2.381 nm^3 in BaF_2 to 2.359 nm^3 in $Ba_{0.93}Y_{0.07}F_{2.07}$. A further increase in the content of the substituent does

not change the size of the unit cells of the obtained solid solutions. This effect may be due to the fact that starting from an yttrium content of 0.07 mol, a second BaF_2 isostructural phase with a lattice period shorter than in the main solid solution begins to form (Fig. 1a). The formation of this phase is observed on the diffraction spectrum of the solid solution with an yttrium content of 0.15 mol; the duplet peaks of the first four diffraction maxima of the main phase are clearly visible, and the intensity of the doublet maxima increases with a corresponding decrease in the intensity of the maxima of the main phase. This means that the second phase is also a solid solution, but with a higher content of yttrium. The crystal lattice of pure YF_3 belongs to the orthorhombic syngony.

The solid solutions obtained at the second stage of synthesis have a tetragonal crystal lattice (P4/nmm) and are isostructural with $BaSnF_4$ (JCPDS card No. 00-038-0738) (Fig. 2a). The maximum content of yttrium in the obtained phases was 0.10 mol. A further increase in the concentration of yttrium in the solid solution causes the evaporation of tin fluoride, a change in the ratio between the components in the system, and the formation of impurity phases.

The calculated volumes of elementary cells of $Ba_{1-x}Y_xSnF_{4+x}$ solid solutions decrease with increasing content of yttrium in the obtained material (Fig. 2b). This dependence can be satisfactorily approximated by a straight line, which is confirmed by the rules of crystallographic substitution.

According to the results of the energy dispersive analysis of the synthesized solid solutions, it was established that the elemental composition of the obtained materi-

Table 1. Elemental composition of $Ba_{1-x}Y_xSnF_{4+x}$ solid solutions

Calculated mixture composition			EDX results after synthesis	
The formula	The element	At., %	At., %	Composition, mole
$BaSnF_4$	Ba	16.66	16.49	0.99
	Sn	16.67	16.84	1.01
	F	66.67	66.67	4.00
$Ba_{0.97}Y_{0.03}SnF_{4.03}$	Ba	15.96	15.87	0.96
	Y	0.50	0.50	0.03
	Sn	16.50	16.69	1.01
	F	67.04	66.94	4.05
$Ba_{0.95}Y_{0.05}SnF_{4.05}$	Ba	15.76	15.87	0.96
	Y	0.82	0.99	0.06
	Sn	16.55	16.20	0.98
	F	66.88	66.94	4.05
$Ba_{0.90}Y_{0.10}SnF_{4.10}$	Ba	14.70	14.77	0.91
	Y	1.64	1.79	0.11
	Sn	16.36	16.07	0.99
	F	67.31	67.37	4.15
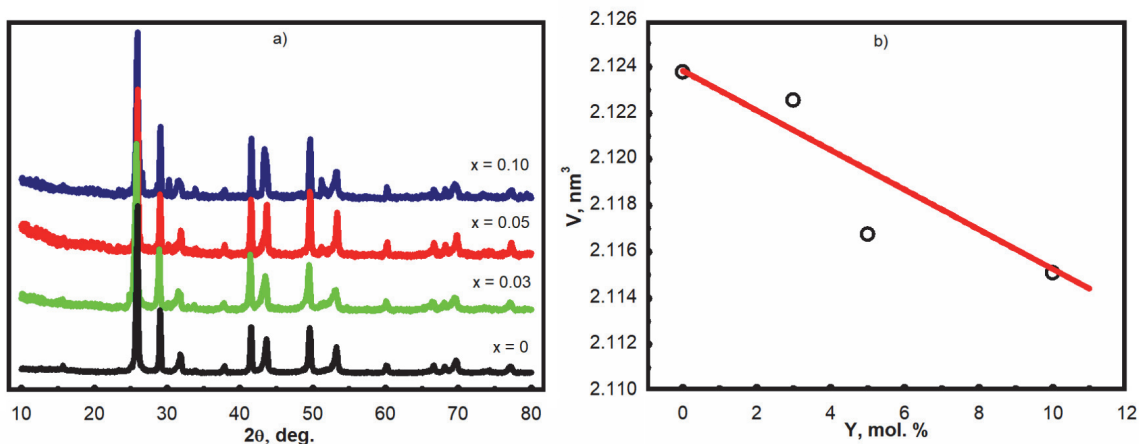
Fig. 2. Diffraction patterns (a) and unit cell volumes (b) of $Ba_{1-x}Y_xSnF_{4+x}$ solid solutions.

als practically does not differ from the calculated (Table 1). Minor deviations from the formula composition observed in the analysis results may be due to the evaporation of SnF_2 and the error of the device.

Studies of the electrical conductivity of the synthesized $Ba_{1-x}Y_xSnF_{4+x}$ solid solutions showed that it improves with an increase in the amount of the substituent in the stoichiometric $BaSnF_4$ compound (Fig. 3). This effect may be due to replacing the nodal positions of Ba^{2+} ions with Y^{3+}; as a result, interstitial F^- ions are formed according to the Kreger-Wink notation:

$$YF_3(BaF_2) \rightarrow Y_{\dot{B}a} + F_i'.$$
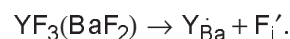
As a result, with an increase in the amount of yttrium in the solid solution, the number of mobile interstitial fluorine anions increases; thus, the conductive properties of the solid electrolyte are improved. The best conductivity values are found for the $Ba_{0.90}Y_{0.10}SnF_{4.10}$ phase, for which $\sigma_{353} = 1.53 \cdot 10^{-3}$ S/cm.

The temperature dependences of the electrical conductivity of the obtained materials are satisfactorily approximated by the Arrhenius-Frenkel equation:

Table 2. Parameters of electrical conductivity of $Ba_{1-x}Y_xSnF_{4+x}$ solid solutions

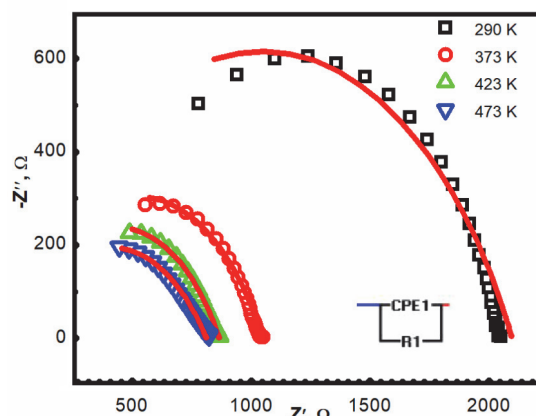| Sample		ΔE_a, eV	lg(A), (S/cm)·K	*sigmaБZZ* sB, S/cm	T, K
BaSnF$_4$	300−430	0.23	1.12	$1.80 \cdot 10^{-5}$	353
	430−623	0.39	3.04	$6.96 \cdot 10^{-4}$	573
Ba$_{0.97}$Y$_{0.03}$SnF$_{4.03}$	300−420	0.11	0.36	$1.46 \cdot 10^{-4}$	353
	420−623	0.32	2.74	$1.54 \cdot 10^{-3}$	573
Ba$_{0.95}$Y$_{0.05}$SnF$_{4.05}$	300−460	0.09	0.48	$4.36 \cdot 10^{-4}$	353
	460−623	0.26	2.31	$1.90 \cdot 10^{-3}$	573
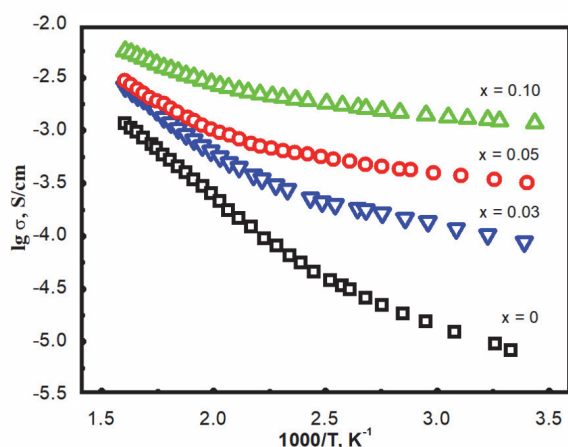
Fig. 3. Temperature dependences of electrical conductivity of $Ba_{1-x}Y_xSnF_{4+x}$ solid solutions.

Fig. 4. Impedance spectra of a Ba$_{0.90}$Y$_{0.10}$SnF$_{4.10}$ solid solution at various temperatures.

$$\sigma T = A\exp(-\Delta E_a / kT), \qquad (1)$$

where A is the pre-exponential factor, ΔE_a is the activation energy of ion conductivity, k is the Boltzmann constant.

Fig. 3 shows that these dependencies are characterized by the presence of two straight sections with different angles of inclination to the temperature axis. This inflection shifts towards higher temperatures from 420 K (for Ba$_{0.97}$Y$_{0.03}$SnF$_{4.03}$) to 465 K (for Ba$_{0.90}$Y$_{0.10}$SnF$_{4.10}$) as the yttrium content in the obtained materials increases. This effect can be associated with structural changes in the solid electrolyte, due to which, as a result of heating the solid electrolyte, the amount of fluorine anions in the interstitial spaces of the crystal lattice increases [14, 16]. Fluoride ions in the conducting phases with the structure of fluorite and tysonite occupy three different positions [6, 17], which differ from each other in the cationic environment and the length of the M−F bond. At a certain tem-

perature, locally mobile fluoride anions acquire enough energy to overcome the energy barrier and move into the interstitial space. With a further increase in temperature, the concentration of charge carriers practically does not change, but only their mobility increases.

The calculated value of the activation energy of the ionic conductivity of the obtained fluoride phases is lower than the corresponding value of the original compound BaSnF$_4$ in the entire temperature range studied (Table 2); this may be due to the influence of the heterovalent substituent on the structure of the solid electrolyte. A gradual decrease in the activation energy from 0.32 eV (for Ba$_{0.97}$Y$_{0.03}$SnF$_{4.03}$) to 0.20 eV (for Ba$_{0.90}$Y$_{0.10}$SnF$_{4.10}$) is observed in the high-temperature region with an increase in the amount of the substituent in the solid solution.

Figure 4 shows the AC impedance spectra of the received electrolyte at different temperatures. The impedance spectra of the Ba$_{0.90}$Y$_{0.10}$SnF$_{4.10}$ solid solution in the Nyquist coordinates are characterized by a depressed semicircular arc (Fig. 4), which is

satisfactorily described by an equivalent circuit in which the volume resistivity R and the constant phase element (CPE) are connected in parallel [18]. The absence of the second high-frequency semicircle on the complex impedance plane indicates the absence of a contribution of surface conductivity to the overall conductivity of polycrystalline samples. For the $Ba_{0.90}Y_{0.10}SnF_{4.10}$ pellet, the impedance decreases with increasing temperature, which means enhanced ionic conductivity.

4. Conclusions

It has been established that up to 0.07 mol of barium ions can be replaced by yttrium in the BaF_2 structure by precipitation from aqueous solutions. As a result, solid solutions with a cubic structure of barium fluoride with a shorter lattice period are formed.

The alloying of $Ba_{1-x}Y_xF_{2+x}$ solid solutions with tin (II) fluoride, results in non-stoichiometric fluoride phases $Ba_{1-x}Y_xSnF_{4+x}$ ($x = 0.03$, 0.05, 0.10) with an isostructural $BaSnF_4$ tetragonal crystal lattice. These solid solutions are characterized by smaller crystal lattice parameters and the presence of mobile interstitial fluorine ions, which have a positive effect on the ionic conductivity.

It was established that with an increase in the amount of yttrium in the $Ba_{1-x}Y_xSnF_{4+x}$ solid solution, the fluoride ion conductivity increases. Thus, the $Ba_{0.90}Y_{0.10}SnF_{4.10}$ phase has the best conducting properties, for which $\sigma = 1.53 \cdot 10^{-3}$ S/cm at 353 K.

Calculations of the conduction activation energy showed that the greater the amount of the substituent in the solid solution, the lower the values of the conduction activation energy of the corresponding phases in the entire temperature range studied.

References

1. V.Kumaravel, J.Bartlett, S.C.Pillai, *Adv. Energy Mater.*, **11**, 2002869 (2020).
2. T.Liu, N.Peng, X.Zhang et al., *Energy Stor. Mater.*, **42**, 42 (2021).
3. M.A.Nowroozi, I.Mohammad, P.Molaiyan et al., *J. Mater. Chem. A*, **9**, 5980 (2021).
4. L.N.Patro, K.Hariharan, *Solid State Ionics*, **239**, 41 (2013).
5. I.Mohammad, R.Witter, M.Fichtner et al., *ACS Appl. Energy Mater.*, **2**, 1553 (2019).
6. K.Mori, A.Mineshige, T.Emoto et al., *J. Phys. Chem. C*, **125**, 12568 (2021).
7. G.Denes, J.Hantash, A.Muntasar et al., *Hyperfine Interact*, **170**, 145 (2006).
8. S.Chaudhuri, F.Wang, C.P.Grey, *J. Am. Chem. Soc.*, **124**, 11746 (2002).
9. L.Liu, L.Yang, M.Liu et al., *Journal of Alloys and Compounds*, **819**, 152983 (2020).
10. L.N.Patro, K.Hariharan, *Ionics*, **19**, 1611 (2013).
11. L.Liu, L.Yang, D.Shao et al., *Ceramics International*, **46**, 20521 (2020).
12. M.M.Ahmad, Y.Yamane, K.Yamada, *Materials Science and Engineering: B*, **178**, 965 (2013).
13. R.N.Pshenichny, Y.V.Pogorenko, T.V.Pavlenko et al., *Voprosy Khimii i Khimicheskoi Tekhnologii*, **1**, 62 (2021).
14. Y.V.Pogorenko, R.M.Pshenychnyi, A.O.Omelchuk et al., *Solid State Ion.*, **338**, 80 (2019)
15. R.D.Shannon, *Acta Cryst.*, **32**, 751 (1976).
16. Sh.Yoshikado, Y.Ito, J.M.Reau, *Solid State Ionics*, **154–155**, 503 (2002).
17. C.Martineau, F.Fayon, C.Legein et al., *Chem. Mater.*, **22**, 1585 (2010).
18. M.Wortmann, N.Frese, A.Mamun et al., *Nanomaterials*, **10**, 1210 (2020).