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Isovalent substitution impact on the structure of two-slab $BaNd_{2-x}Sm_xIn_2O_7$ indates

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The conditions of isovalent substitution of Nd atoms by Sm atoms in *A*-positions of the $BaNd_2In_2O_7$ two-slab perovskite-like structure of the $BaNd_{2-x}Sm_xIn_2O_7$ type ($0 \leq x \leq 1.8$) have determined by X-ray powder diffraction methods. Tetragonal crystal structure (space group *P4₂/mnm*) of the $BaNd_{2-x}Sm_xIn_2O_7$ phases with substitution degree of Nd atoms equal to 0.5, 1.0, 1.5 and 1.8 was determined by the Rietveld method. Crystal structure of $BaNd_{2-x}Sm_xIn_2O_7$ is based on the two-dimensional (infinite in the *XY* plane) perovskite-like blocks, consisting of two slabs of the deformed InO_6 octahedra connected by vertices. Ba atoms are localized only at 4*f* position inside the perovskite block, while REE atoms are placed only at 8*j* position at the boundary of the perovskite block. The adjacent perovskite-like blocks are separated by a slab of LnO_9 polyhedra and held together by - O - Ln - O - interblock bonds. It is established that the isovalent substitution of Nd atoms by smaller Sm atoms leads to a decrease in the length of the Ln - O2 interblock distance (from 0.230(2) nm to 0.206(2) nm) and to an increase in the degree of deformation of the interblocks of LnO_9 polyhedra, the inner block polyhedra BaO_{12}, and the InO_6 octahedra as well. Such structural changes destabilize the interblock "stitching" and are one of the main destruction factors of the slab perovskite-like structure (SPS) of the $BaNd_{2-x}Sm_xIn_2O_7$ phases at $x > 1.8$. Data obtained could be used for directed regulation of structure-sensitive properties of materials based on the $BaNd_2In_2O_7$ indate.

Keywords: compounds of $A_{n+1}B_nO_{3n+1}$ – type, slab perovskite-like structure, X-ray powder diffraction, isomorphism, solid solutions.

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Introduction

A family of An+1BnO3n+1 type compounds (A = Sr, Ba, Ca, Ln, Na, K; B = Al, Ga, Fe, Ni, Cr, Sc, In, Ti, Sn, Zr, Hf, Pb, Mn; n is the number of BO6 octahedron slabs in the block, varies from 1 to 3) occupies a special place among the homologous series of compounds with SPS due to a set of electrophysical, optical and catalytic properties [1-8]. One of the common ways to regulate the characteristics of oxide compounds and oxide-based materials is the isomorphic substitution of atoms in different crystallographic positions. The impact of such substitution on the structure of $A_{n+1}B_nO_{3n+1}$ compounds has been established in sufficient detail for Sr - containing $A_{n+1}B_nO_{3n+1}$ compounds with SPS [9,10].

It should be noted that for Ba, Ln-containing representatives of the $A_{n+1}B_nO_{3n+1}$ family with two-slab SPS the composition/structure relation has predominantly established for La-containing compounds such as $BaLa_{2-x}Sm_xIn_2O_7$ [11], $BaLa_{2-x}Dy_xSc_2O_7$ [12], $Ba_{1-x}Sr_xLa_2In_2O_7$ [13], as well as for $Ba_{1-x}Sr_xNd_2In_2O_7$ [14].

$BaNd_2In_2O_7$ indate among the known $BaLn_2In_2O_7$ (Ln = La – Nd) two-slab indates [15,16] is characterized by the largest size mismatch of A- and B-sublattices of the SPS, which has a significant impact on the properties of individual compounds and isomorphosubstituted phases based on them.

The interblock slab of NdO_9 polyhedra in SPS of

$BaNd_2In_2O_7$ "stitches" the adjacent two-slab perovskite-like blocks together. However, the nature of the isovalent substitution of Nd atoms on the structure features of $BaNd_2In_2O_7$-based SPS phases has remained unclear up to now.

The purpose of this work is to determine the conditions of isovalent substitution of Nd atoms in $BaNd_2In_2O_7$ SPS of the $BaNd_{2-x}Sm_xIn_2O_7$ and to study its influence on the structure of the two-slab perovskite structure of $BaNd_{2-x}Sm_xIn_2O_7$ indates.

I. Materials and methods

Synthesis of $BaNd_{2-x}Sm_xIn_2O_7$ indates was carried out by co-crystallization (evaporation with vigorous stirring) of a mixture of aqueous solutions of Ba, Nd, Sm and In salts with a ratio of Ba:Nd:Sm: In = 1:2 – x:x:2, followed by a heat treatment of product synthesized on a gas burner to remove the bulk of nitrogen oxides. The mixture obtained in this way was ground, pressed in the form of disks and subjected to a heat treatment at 1570K to achieve a constant phase composition. Chemically pure (≥ 99 wt. %) nitrates of Nd, Sm, In and acetate of Ba were used as starting reagents in the work.

X-ray diffraction spectra of polycrystalline samples were recorded on a Shimadzu XRD-6000 diffractometer in discrete mode (scanning step was equal to 0.02°, exposure at a point was 7 seconds, angle interval 2θ = 20 - 75°) on a copper filtered $CuK\alpha$ radiation (arc graphite monochromator in front of the counter).

Crystal structure of the samples was determined by the Rietveld method. Primary processing of diffraction spectra and structural calculations were performed using a hardware-software complex, as described in [17].

Second harmonic generation test of laser radiation by $BaNd_{2-x}Sm_xIn_2O_7$ powders was performed according to the Kurtz-Perry method [18,19]. An Nd:YAG laser was used as a radiation source (λ_ω=1064 nm, $\lambda_{2\omega}$=532 nm, repetition frequency 12.5 Hz in Q-modulation mode).

II. Experimental results

The results of X-ray phase analysis of heat-treated samples of co-crystallized salts showed that the phases of $BaNd_{2-x}Sm_xIn_2O_7$ with SPS exist in the concentration range of $0 \le x \le 1.8$. The destruction of SPS begins with further increase in the degree of substitution of Nd atoms by Sm atoms in two-slab indates $BaNd_{2-x}Sm_xIn_2O_7$ with the formation of $(Sm,Nd)InO_3$ phase with rhombic perovskite structure and $Ba(Sm,Nd)InO_4$ phase with $CaFe_2O_4$ type structure, where Sm, Nd and In atoms are simultaneously located in B-position.

The X-ray diffraction patterns of $BaNd_{2-x}Sm_xIn_2O_7$ indates with SPS are similar to the diffraction patterns of two-slab $BaNd_2In_2O_7$ [15] and the indexing showed that their crystal structure belongs to the tetragonal syngony. Systematics of attenuation of reflections on $BaNd_{2-x}Sm_xIn_2O_7$ with SPS X-ray diffraction patterns indicates the following possible space groups: centrosymmetric $P4_2/mnm$ and noncentric asymmetric $P4_2nm$ or $P\bar{4}n2$. Results of the test for the generation of the second harmonic signal of the Nd:YAG laser radiation showed that the relative intensity of of $I_{2\omega}$ signal for $BaNd_{2-x}Sm_xIn_2O_7$ ($0 \le x \le 1.8$) does not exceed 0.01 $I_{2\omega}$ for the non-centrosymmetric compound of $La_4Ti_4O_{14}$ with SPS. Such a small value of $I_{2\omega}$ clearly indicates that the SPS of $BaNd_{2-x}Sm_xIn_2O_7$ phases (as well as the original $BaNd_2In_2O_7$ compound) belongs to the centrosymmetric $P4_2/mnm$ space group.

Linear dependences of the periods and volumes of the elementary cells of the $BaNd_{2-x}Sm_xIn_2O_7$ phases with SPS on the substitution degree of Nd atoms (Fig. 1) allows referring them to a limited number of solid solutions.

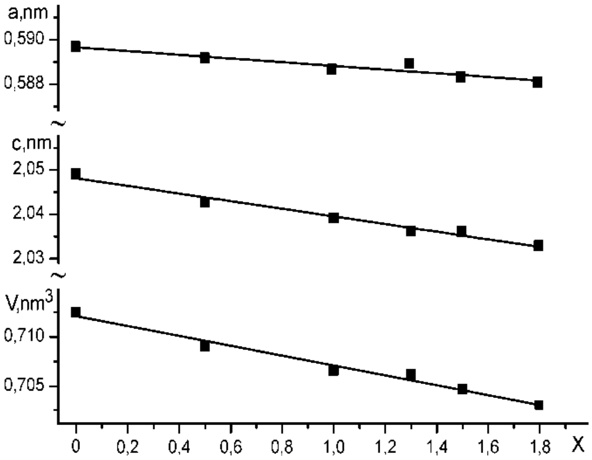

Fig. 1. Dependences of parameters and volumes of elementary cells of $BaNd_{2-x}Sm_xIn_2O_7$ phases on the substitution degree of Nd atoms (*x* values).

Considering the isostructural nature of $BaNd_{2-x}Sm_xIn_2O_7$ indates ($0 \le x \le 1.8$) with SPS, the initial estimation of atomic coordinates for the original models of $BaNd_{2-x}Sm_xIn_2O_7$ structures was performed according to the known structural data for $BaNd_2In_2O_7$ [15] (sp. gr. $P4_2/mnm$). Comparison of experimental and calculated intensity for such structural models showed their satisfactory convergence. The results of the models' refinement of the structure of $BaNd_{2-x}Sm_xIn_2O_7$ phases (x=0.5, 1.0, 1.5, 1.8) and their diffraction data are presented in s 1–3 and on Fig. 2. Phase compositions of $BaNd_{2-x}Sm_xIn_2O_7$ with SPS specified at the structural calculation correspond to the experimental set within error.

Unfortunately, it is impossible to determine Ba, Nd and Sm atoms localization in $BaNd_{2-x}Sm_xIn_2O_7$ SPS using diffractometric data due to the proximity of their atomic scattering factors. Determination of Ba, Nd and Sm atoms distribution between 4f and 8j crystallographic positions in $BaNd_{2-x}Sm_xIn_2O_7$ SPS was performed by calculating the bond valence sums (BVS) of these atoms in the BaO_9, BaO_{12} and $(Nd_{2-x}Sm_x)O_9$, $(Nd_{2-x}Sm_x)O_{12}$ polyhedra (4).

The bond valence (s) Me - O was calculated by the formula $s = \exp((R_0 - R)/B)$ [21], where: R_0 is the tabulated value of the monovalent bond length, R is the experimental value of the bond length, and B is the tabulated value of the variance of the bond lengths, which was used to find R_0 and is equal to 0.037 nm. The bond valence sums were found by summing the valences of all the bonds: $BVS = \Sigma s \cdot n$, where n is the number of bonds of this type. When the atoms of Nd and Sm were in the same position at the same time, the standard value of R_0 was adjusted by the equation:

$R_0 = R_0(Nd) \cdot K(Nd) + R_0(Sm) \cdot K(Sm)$, where $R_0(Nd)$ and $R_0(Sm)$ are the tabulated values of the monovalent bond length, and K(Nd) and K(Sm) are the values of filling this position.

As follows from 4, BVS values of Ba and REE atoms in the hypothetical BaO_9 and LnO_{12} polyhedra significantly differ from their chemical valences, while BVS values of these elements are much closer to their valences if Ba atoms localize in 4f and REE atoms localize in 8j position.

The obtained results of BVS calculations indicate a completely ordered arrangement of Ba and REE atoms in $BaNd_{2-x}Sm_xIn_2O_7$ SPS with localization of Ba atoms only in intrablock cuboctahedral voids of the perovskite-like block (BaO_{12} polyhedron) and REE atoms only in LnO_9 polyhedra at the block boundary. The probable reason for this distribution of Ba and REE atoms in the two-slab SPS $BaNd_{2-x}Sm_xIn_2O_7$ is, apparently, the tendency of relatively small REE atoms to occupy smaller MeO_9 polyhedra.

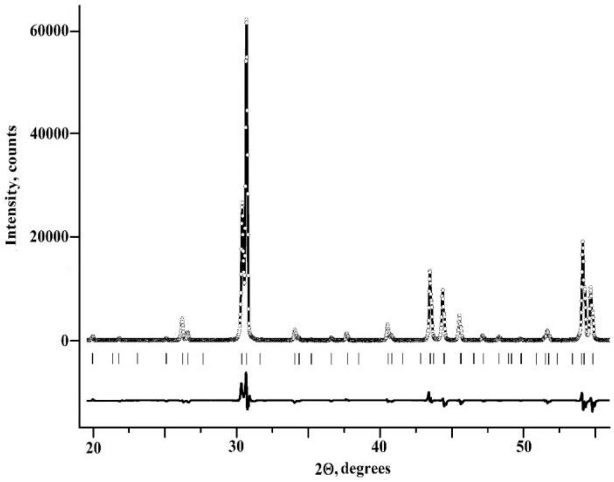

Fig. 2. Experimental (circles), calculated (solid) and difference diffraction patterns of $BaNd_{0.5}Sm_{1.5}In_2O_7$ (CuK_α radiation).

Table 1

Structural data of $BaNd_{2-x}Sm_xIn_2O_7$ (sp. gr. *P4₂/mnm* (136)).

x	Parameters of crystal lattice (nm)	Independent reflections	Total isotropic factor *B* (nm^2)	Texture parameter	Reliability factor, R_w
0.5	*a* = 0.58918(9) *c* = 2.0427(3)	86	$0.43(3) \cdot 10^{-2}$	0.430(4) [001] texture axis	0.033
1.0	*a* = 0.58865(2) *c* = 2.0391(1)	86	$0.12(3) \cdot 10^{-2}$	0.724(7) [001] texture axis	0.032
1.5	*a* = 0.58831(6) *c* = 2.0360(1)	86	$0.10(4) \cdot 10^{-2}$	0.678(7) [001] texture axis	0.035
1.8	*a* = 0.58807(2) *c* = 2.0328(1)	86	$0.39(3) \cdot 10^{-2}$	0.638(6) [001] texture axis	0.035

Table 2

Coordinates of atoms in SPS of $BaNd_{2-x}Sm_xIn_2O_7$.

Position	Atom	$BaNd_{1,5}Sm_{0,5}In_2O_7$				$BaNdSmIn_2O_7$			
		Position filling	*X*	*Y*	*Z*	Position filling	*X*	*Y*	*Z*
4*f*	Ba	1	0.2585(2)	*X*	0	1	0.2599(3)	*X*	0
8*j*	Nd	0.75	0.2755(2)	*X*	0.1854(2)	0.5	0.2760(2)	*X*	0.1854(2)
	Sm	0.25				0.5			
8*j*	In	1	0.2621(3)	*X*	0.3960(3)	1	0.2609(2)	*X*	0.3961(3)
4*g*	O1	1	0.780(2)	1-*X*	0	1	0.775(3)	1-*X*	0
8*j*	O2	1	0.188(2)	*X*	0.285(3)	1	0.185(2)	*X*	0.282(3)
8*h*	O3	1	0	0.5	0.103(2)	1	0	0.5	0.091(2)
4*e*	O4	1	0	0	0.141(2)	1	0	0	0.147(2)
4*e*	O5	1	0	0	0.371(3)	1	0	0	0.374(3)
Position	Atom	$BaNd_{0,5}Sm_{1,5}In_2O_7$				$BaNd_{0,2}Sm_{1,8}In_2O_7$			
		Position filling	*X*	*Y*	*Z*	Position filling	*X*	*Y*	*Z*
4*f*	Ba	1	0.2619(2)	*X*	0	1	0.2558(3)	*X*	0
8*j*	Nd	0.25	0.2791(3)	*X*	0.1859(2)	0.1	0.2775(3)	*X*	0.1862(2)
	Sm	0.75				0.9			
8*j*	In	1	0.2590(2)	*X*	0.3965(2)	1	0.2645(2)	*X*	0.3960(3)
4*g*	O1	1	0.770(2)	1-*X*	0	1	0.775(2)	1-*X*	0
8*j*	O2	1	0.184(2)	*X*	0.281(2)	1	0.185(3)	*X*	0.280(2)
8*h*	O3	1	0	0.5	0.091(2)	1	0	0.5	0.092(2)
4*e*	O4	1	0	0	0.150(3)	1	0	0	0.148(2)
4*e*	O5	1	0	0	0.377(2)	1	0	0	0.378(3)

The main structural elements of the $BaNd_{2-x}Sm_xIn_2O_7$ indates with SPS are the unconnected two-dimensional (infinite in the XY plane) perovskite-like blocks, each of which consists of two slabs of deformed InO_6 octahedra (Fig. 3a).

InO6 octahedra are connected in blocks only by vertices so that each octahedron has five common vertices with adjacent octahedra of the same block. In the diagonal direction of XY plane, the adjacent blocks are offset by half-edges of the perovskite cube and alternate with each other. A slab of LnO_9 polyhedra is located between adjacent perovskite-like blocks and the blocks are held together by - O - Ln - O - interblock bonds. Eight of nine oxygen atoms (four O2, two O3, one O4 and one O5) of the LnO_9 polyhedron belong to the same block as Ln atoms, and the ninth oxygen atom (O2) belongs to the adjacent block (Fig. 3b). This Ln - O2 interblock bond is the shortest among all LnO_9 polyhedron bonds (0.223(2)-0.206(2) nm, 3) and its length is close to the minimum known Ln - O distances. This highlights the fact that big Ba atoms cannot occupy the position 8j in MeO9 polyhedra between the perovskite-like blocks and confirms the conclusion made from BVS calculations that they are localized only at position 4f in the great intrablock voids of the perovskite-like block, where their coordination polyhedron is a deformed BaO_{12} cuboctahedron. It should be noted that two O_2 atoms in the LnO_9 polyhedron are located much further (0.352(3) - 0.357(3) nm) (3) from the REE atom than the other oxygen atoms, so the coordination number of REE atoms can be interpreted as 7 + 2.

Analysis of the deformation degree of $(Nd,Sm)O_9$ polyhedra and the length of the (Nd,Sm) - O2 interblock bonds $BaNd_{2-x}Sm_xIn_2O_7$ with SPS shows that the substitution of Nd atoms by smaller Sm atoms leads to quite significant (from $279\cdot10^{-4}$ to ~$340\cdot10^{-4}$) increase in the deformation degree of the $(Nd,Sm)O_9$ interblock polyhedra as well as a significant decrease in the length of the (Nd,Sm) - O2 interblock bond (from 0.223(2) nm to 0.206(2) nm) (Fig. 4a , 3). It should be noted that the value of the deformation degree of $(Nd,Sm)O_9$ interblock polyhedra for phases with the maximum substitution degree of Nd atoms (~$340\cdot10^{-4}$) is close to the maximum known for compounds of the $A_{n+1}B_nO_{3n+1}$ type with SPS. Such changes in the structure of $BaNd_{2-x}Sm_xIn_2O_7$ with SPS increase the strain of the interblock space and bring its structure closer to the three-dimensional structure of the perovskite and are obviously one of their main factors limiting ($0\leq x\leq1.8$) the size of the existing region of $BaNd_{2-x}Sm_xIn_2O_7$ phase with SPS and the absence of the

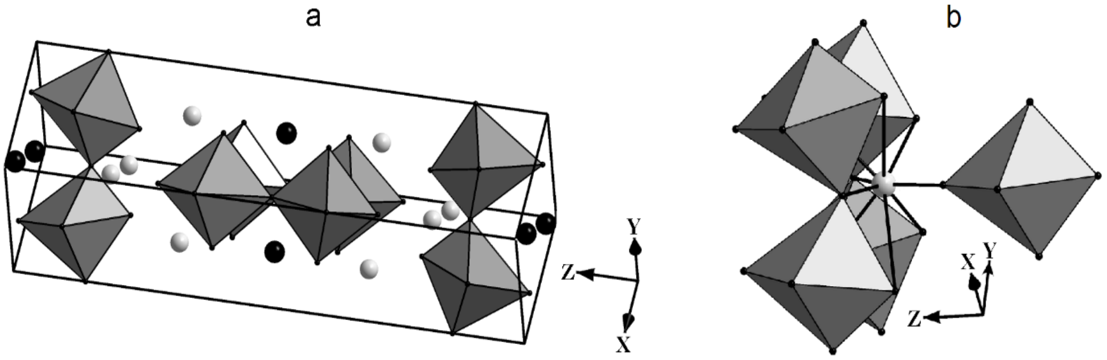

Fig. 3. Crystal structure of $BaNd_{1.5}Sm_{0.5}In_2O_7$ in the form of InO_6 octahedra and Nd, Sm atoms (light circles) and Ba (dark circles) (a) and the structure of the interblock boundary in $BaNd_{0.5}Sm_{1.5}In_2O_7$ with SPS in the form of InO_6 octahedra and Nd, Sm atoms (gray circle) (b).

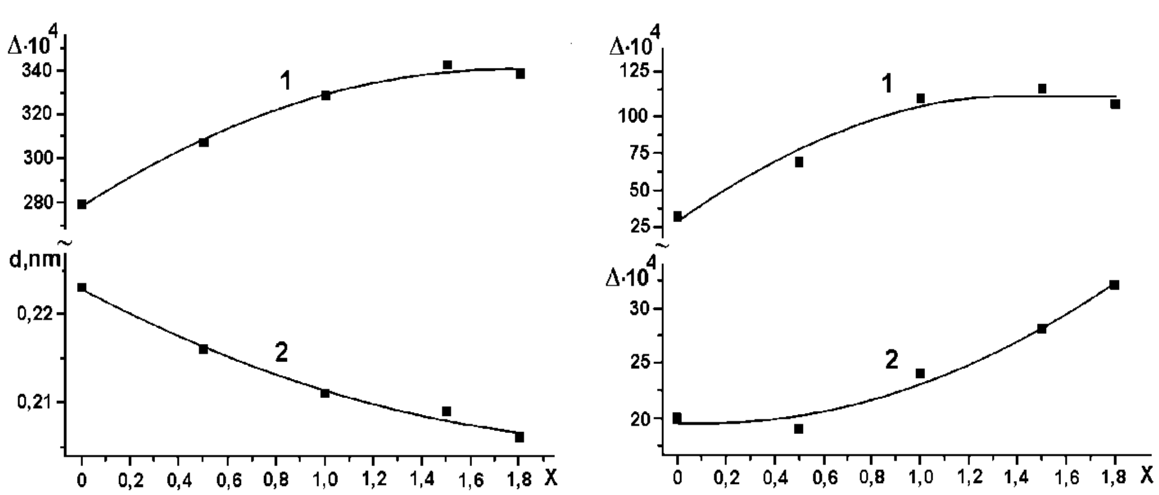

Fig. 4. Dependences of the deformation degree (Δ) of $(Nd,Sm)O_9$ polyhedra(1) and the length of (Nd,Sm) - O_2 (2) interblock bond in $BaNd_{2-x}Sm_xIn_2O_7$ with SPS on the substitution degree of Nd atoms (value *x*) (a); dependences of the deformation degree (Δ) of BaO_{12}(1) and InO_6 (2) polyhedra in the SPS of $BaNd_{2-x}Sm_xIn_2O_7$ on the substitution degree of Nd atoms (value *x*) (b).

Table 3

Interatomic distances (d), deformation degree (Δ) of of polyhedra BaO_{12}, NdO_9, $(Nd,Sm)O_9$ and InO_6 in SPS $BaNd_2In_2O_7$ and $BaNd_{2-x}Sm_xIn_2O_7$.

$BaNd_2In_2O_7$ [15]		Atoms	$x = 0.5$	$x = 1.0$	$x = 1.5$	$x = 1.8$
Atoms	d, nm		d, nm	d, nm	d, nm	d, nm
Ba – 2O1	0.286(3)	Ba - 2O1	0.283(2)	0.286(1)	0.290(2)	0.283(2)
Ba – 4O3	0.306(2)	Ba - 4O3	0.296(2)	0.279(2)	0.279(2)	0.280(1)
Ba – 2O1	0.306(3)	Ba - 2O1	0.308(2)	0.304(2)	0.300(2)	0.306(3)
Ba – 2O5	0.295(2)	Ba – 2O5	0.332(3)	0.326(3)	0.319(2)	0.321(2)
Ba – 2O4	0.342(1)	Ba – 2O4	0.360(3)	0.370(2)	0.375(3)	0.369(3)
Ba – O_{aver}	0.307	$(Ba – O)_{aver}$	0.312	0.307	0.307	0.307
Δ BaO_{12}	$32 \cdot 10^{-4}$	Δ BaO_{12}	$69 \cdot 10^{-4}$	$112 \cdot 10^{-4}$	$118 \cdot 10^{-4}$	$108 \cdot 10^{-4}$
Nd – 1O2*	0.223(2)	(Nd,Sm) – 1O2*	0.216(1)	0.211(1)	0.209(2)	0.206(2)
Nd – 1O5	0.248(1)	(Nd,Sm) – 1O5	0.220(2)	0.222(1)	0.224(2)	0.226(2)
Nd – 2O2	0.247(1)	(Nd,Sm) – 2O2	0.251(2)	0.251(2)	0.249(1)	0.250(2)
Nd – 1O4	0.258(1)	(Nd,Sm) – 1O4	0.247(1)	0.243(2)	0.243(2)	0.243(1)
Nd – 2O3	0.262(3)	(Nd,Sm) – 2O3	0.269(2)	0.284(3)	0.285(2)	0.284(3)
Nd – 2O2	0.356(2)	(Nd,Sm) – 2O2	0.352(3)	0.355(2)	0.357(3)	0.356(2)
Nd - O_{aver}	0.273	$((Nd,Sm) – O)_{aver}$	0.270	0.273	0.273	0.273
Δ NdO_9	$279 \cdot 10^{-4}$	Δ $(Nd,Sm)O_9$	$307 \cdot 10^{-4}$	$328 \cdot 10^{-4}$	$342 \cdot 10^{-4}$	$338 \cdot 10^{-4}$
In – 1O4	0.210(1)	In – 1O4	0.212(2)	0.218(2)	0.222(2)	0.215(2)
In – 2O3	0.209(2)	In – 2O3	0.209(1)	0.210(1)	0.210(2)	0.210(1)
In – 1O1	0.210(1)	In – 1O1	0.213(2)	0.212(1)	0.211(1)	0.212(2)
In – 1O5	0.215(2)	In – 1O5	0.224(2)	0.222(2)	0.219(2)	0.223(2)
In – 1O2	0.236(2)	In – 1O2	0.235(2)	0.241(1)	0.243(1)	0.245(2)
In – O_{aver}	0.215	In – O_{aver}	0.217	0.219	0.219	0.219
Δ InO_6	$20 \cdot 10^{-4}$	Δ InO_6	$19 \cdot 10^{-4}$	$24 \cdot 10^{-4}$	$28 \cdot 10^{-4}$	$32 \cdot 10^{-4}$

Notes: the calculation of the deformation degree of MeO_n polyhedra is performed by the formula: $\Delta = 1/n \sum [(R_i - \bar{R})/\bar{R}]^2$ (R_i is the distance *Me* - O, $\bar{R}$ is the average distance *Me* - O, n is the coordination number) [20]; * is the interblock distance.

Table 4

The calculated values of bond valence sums for Ba and REE atoms in MeO_n polyhedra of SPS $BaNd_2In_2O_7$ and $BaNd_{2-x}Sm_xIn_2O_7$.

x	R_0 $(Nd_{2-x}Sm_x)$, nm	BVS			
		Position 4*f*		Position 8*j*	
		Polyhedron		Polyhedron	
		BaO_{12}	LnO_{12}	BaO_9	LnO_9
0 [15]	0.2105	1.59	0.98	4.29	2.64
0.5	0.210075	1.52	0.92	5.10	3.10
1.0	0.20965	1.89	1.14	5.07	3.05
1.5	0.209225	1.90	1.13	5.14	3.06
1.8	0.20897	1.91	1.12	5.21	3.07

Note. The value of R_0 for the Ba - O bond is 0.2285 nm, for the Nd - O bond R_0 = 0.2105 nm, for the Sm - O bond R_0 = 0.2088 nm [21].

$BaSm_2In_2O_7$ compound. The localization of smaller Sm atoms in the $(Nd,Sm)O_9$ interblock polyhedra also affects the structure of the perovskite-like SPS block, namely, it increases the deformation of BaO_{12} intrablock polyhedra and InO_6 octahedra (Fig. 4b, 3).

The revealed structure/composition correlations for $BaNd_{2-x}Sm_xIn_2O_7$ are generally similar to those for single $BaLn_2In_2O_7$ (Ln = La, - Nd) indates [15] and phases based on them. In particular, as can be seen from Fig. 5 and 5, the decrease of the crystal ionic radius of interblock REE atoms in $BaLn_2In_2O_7$, $Ba_{1-x}Sr_xLn_2In_2O_7$, and $BaLn_{2-x}Ln^I_xIn_2O_7$ leads to a gradual decrease in the length of the Ln – O2 interblock bond and to an increase in the deformation degree of LnO_9 interblockpolyhedra. At the same time, it should be noted that the most extreme values of ΔLnO_9 and the interblock Ln – O_2 distance in the SPS of $BaNd_{2-x}Sm_xIn_2O_7$ phases may indicate the advanced level of properties of these phases.

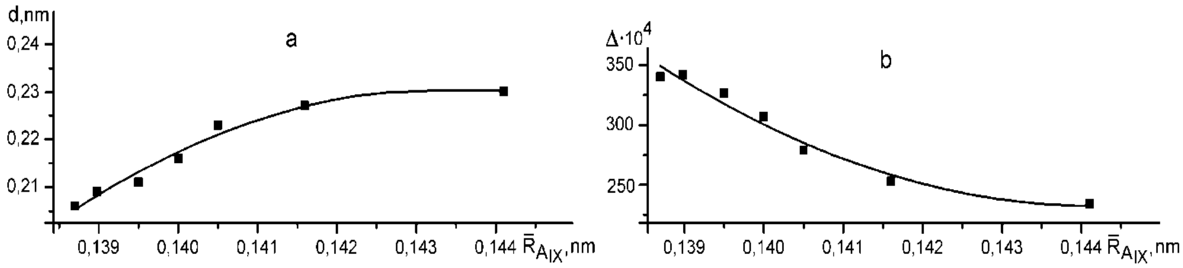

Fig. 5. Dependences of the length of Ln - O2 interblock bond (a) and the deformationdegree (Δ) of LnO_9 polyhedra (b) on the value of average crystalline ionic radius of REE atoms in SPS $BaLn_2In_2O_7$ (Ln = La, Pr, Nd) and $BaNd_{2-x}Sm_xIn_2O_7$.

Table 5

Some structural data of $BaLn_2In_2O_7$, $Ba_{1-x}Sr_xLn_2In_2O_7$ and $BaLn_{2-x}Ln^I_xIn_2O_7$ with SPS.

Composition	Space group	Value *x*	$\Delta LnO_9\cdot10^4$	Interblock distance	
$BaLn_2In_2O_7$ [15]	*P4₂/mnm*	La - Nd	234-279	Ln – O_2	0.230(2) - 0.223(2)
$Ba_{1-x}Sr_xLa_2In_2O_7$[13]	*P4₂/mnm*	$x = 0$	234	La – O_2	0.230(2)
	Fmmm	$0 < x \le 0.75$	74 - 90	La2 – O_2	0.238(2) - 0.215(2)
$Ba_{1-x}Sr_xNd_2In_2O_7$ [14]	*P4₂/mnm*	**$0 \le x \le 0.2$**	279 - 287	Nd – O_2	0.223(2) - 0.214(1)
$BaLa_{2-x}Sm_xIn_2O_7$ [11]	*P4₂/mnm*	$0 \le x \le 1.8$	234 - 250	Ln – O_2	0.230(2) - 0.214(1)
$BaNd_{2-x}Sm_xIn_2O_7$	*P4₂/mnm*	$0 \le x \le 1.8$	279 - 340	Ln – O_2	0.223(2) - 0.206(2)

Conclusions

Thus, in this paper the conditions of isovalent substitution of Nd atoms by Sm atoms in two-slab SPS of $BaNd_2In_2O_7$ indate of $BaNd_{2-x}Sm_xIn_2O_7$ type are established and the structure of SPS phases $BaNd_{1.5}Sm_{0.5}In_2O_7$, $BaNdSmIn_2O_7$, $BaNd_{0.5}Sm_{1.5}In_2O_7$ and $BaNd_{0.2}Sm_{1.8}In_2O_7$ has defined by the Rietveld method.

Analysis of the obtained results has revealed the relation between structure features of the SPS phases $BaNd_{2-x}Sm_xIn_2O_7$ (the length of Ln - O2 interblock bonds, the deformation degree of the LnO_9 interblock polyhedra, BaO_{12} intrablock polyhedra and InO_6 octahedra) and the degree of isovalent substitution of Nd atoms.

The results obtained can be used to regulate the structurally dependent (luminescent, electrophysical and other) properties of materials based on $BaNd_2In_2O_7$ indate.

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[1] P. Ding, W. Li, H. Zhao, C. Wu, L. Zhao, B. Dong, S. Wang, *Review on Ruddlesden–Popper Perovskites as Cathode for Solid Oxide Fuel Cells*, J. Phys.: Mater., 4(2), 022002 (2021); https://iopscience.iop.org/article/10.1088/2515-7639/abe392/pdf.

[2] S. Kamimura, H. Yamada, Chao-Nan Xu, *Strong Reddish-Orange Light Emission from Stress-Activated $Sr_{n+1}Sn_nO_{3n+1}$:Sm^{3+} (n = 1, 2, ∞) with perovskite-related structures*, Appl. Phys. Lett., 101 (9), 91 (2012); https://doi.org/10.1063/1.4749807.

[3] I.S. Kim, T. Nakamura, M. Itoh, J. Ceram, *Humidity Sensing Effects of the Layered Oxides SrO $(LaScO_3)_n$ (n=1, 2, ∞)*, Soc. Jap., 101 (1175), 800 (1993); https://doi.org/10.2109/jcersj.101.800.

[4] S. Kato, M. Ogasawara, M. Sugai, S. Nakata, *Synthesis and Pxide Ion Conductivity of New Layered Perovskite $La_{1-x}Sr_{1+x}InO_{4-d}$*, Sol. St. Ionics, 149(1-2), 53 (2002); https://doi.org/10.1016/s0167-2738(02)00138-8.

[5] G. Nirala, D. Yadav, S. Upadhyay, *Ruddlesden-Popper Phase A_2BO_4 Oxides: Recent Studies on Structure, Electrical, Dielectric, and Optical Properties*, J. Advanced Ceramics, 9(2), 129 (2020); https://doi.org/10.1007/s40145-020-0365-x.

[6] K. Shimizu, S. Itoh, T. Hatamachi, T. Kodama, M. Sato, K. Toda, *Photocatalytic Water Splitting on Ni-Intercalated Ruddlesden−Popper Tantalate $H_2La_{2/3}Ta_2O_7$*, Chem. Mater., 17(20), 5161 (2005); https://doi.org/10.1021/cm050982c.

[7] Y.S. Zhen, J.B. Goodenough, *Oxygen-Ion conductivity in* $Ba_8In_6O_{17}$, Mater. Res. Bull., 25(6), 785 (1990); https://doi.org/10.1016/0025-5408(90)90207-I.

[8] R.E. Schaak, T.E. Mallouk, *Perovskites by Design: A Toolbox of Solid-State Reactions*, Chem. Mater., 14(4), 1455 (2002); https://doi.org/10.1021/cm010689m.

[9] Y.A. Titov, N.M. Belyavina, M.S. Slobodyanik, V.V. Chumak, O.I. Nakonechna, *Synthesis and Crystal Structure of Isovalently Substituted Slab* $SrLa_{2-x}Dy_xSc_2O_7$ *Scandates*, Voprosy Khimii i Khimicheskoi Tekhnologii, (6), 228 (2019); https://doi.org/10.32434/0321-4095-2019-127-6-228-235.

[10] Y.A. Titov, N.N. Belyavina, M.S. Slobodyanik, V.V, Chumak, O.I. Nakonechna, *Features of the* $SrLa_2Sc_{2-x}In_xO_7$ *Two-Slab Structure*, Voprosy Khimii i Khimicheskoi Tekhnologii, (2), 118 (2020); (http://dx.doi.org/10.32434/0321-4095-2020-129-2-118-124).

[11] Y. Titov, N. Belyavina, M. Slobodyanik, O. Nakonechna, N. Strutynska, M. Tymoshenko, Open Chemistry, Effect of Isovalent Substitution on the Crystal Structure and Properties of Two-Slab Indates $BaLa_{2-x}Sm_xIn_2O_7$ 18(1), 1294 (2020); https://doi.org/10.1515/chem-2020-0090.

[12] Y.A. Titov, V.V, Chumak, M.V. Tymoshenko, *Synthesis and Crystal Structure of Two-Slab Scandates* $BaLa_{2-x}Dy_xSc_2O_7$, Reports of the National Academy of Sciences of Ukraine, (3), 68 (2022); https://doi.org/10.15407/dopovidi2022.03.068.

[13] Y.A. Titov, N.N. Belyavina, M.S. Slobodyanik, V.V, Chumak, *Crystal Structure of Isovalent Substituted Layered Indates* $Ba_{1-x}Sr_xLa_2In_2O_7$, Reports of the National Academy of Sciences of Ukraine, (6), 95 (2016); (https://doi.org/10.15407/dopovidi2016.06.095).

[14] Y.A. Titov, N.N. Belyavina, M.S. Slobodyanik, O.I. Nakonechna, N.Yu. Strutynska, *Synthesis and Crystal Structure of Two-Slab* $Ba_{1-x}Sr_xNd_2In_2O_7$ *indates*, Physics and Chemistry of Solid State, 23(2), 375 (2022); https://doi.org/10.15330/pcss.23.2.375-379.

[15] Y.A. Titov, N.M. Belyavina, V.Y. Markiv, M.S. Slobodyanik, Y.A. Kraevska, V.P. Yaschuk, *Synthesis and Crystal Structure of* $BaLn_2In_2O_7$, Reports of the National Academy of Sciences of Ukraine, (1), 148 (2010); http://dspace.nbuv.gov.ua/handle/123456789/19268.

[16] M. Caldes, C. Michel, T. Rouillon, M. Hervieu, B. Raveau, *Novel Indates* $Ln_2BaIn_2O_7$, *n = 2 Members of the Ruddlesden-Popper Family (Ln = La, Nd)*, J. Mater. Chem. 12(3), 473 (2002); https://doi.org/10.1039/B108987K.

[17] M. Dashevskyi, O. Boshko, O. Nakonechna, N. Belyavina, *Phase Transformations in Equiatomic Y–Cu Powder Mixture at Mechanical Milling*, Mettalofizika Noveishie Tekhnologii, 39(4), 541 (2017); https://doi.org/10.15407/mfint.39.04.0541.

[18] S.K. Kurtz, T.T. Perry, A Powder Technique for the Evaluation of Nonlinear Optical Materials, J. Appl. Phys. 39(8), 3798 (1968); https://doi.org/10.1063/1.1656857.

[19] S.K. Kurtz, J.P. Dougherty, *Methods for the detection of noncen-trosymmetry in solids. In: Systematic Matersals Analysis, V. IV, chapter*, 38 p. 269—342 (Academic Press, New York, 1978); https://doi.org/10.1016/B978-0-12-587804-3.50017-0.

[20] R.D. Shannon, *Revised Effective Ionic Radii and Systematic Studies of Interatomic Distances in Halides and Chalcogenides*, Acta Crystallographica A, 32, 751 (1976); https://doi.org/10.1107/S0567739476001551.

[21] I.D. Brown, D. Altermatt, *Bond-Valence Parameters Obtained from a Systematic Analysis of the Inorganic Crystal Structure Database*, Acta Crystallographica B, 41(4), 244 (1985); https://doi.org/10.1107/S0108768185002063.

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Вплив ізовалентного заміщення на будову двошарових індатів $BaNd_{2-x}Sm_xIn_2O_7$

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Методами рентгенівської порошкової дифракції встановлені умови ізовалентного заміщення атомів Nd на атоми Sm в *A*-позиції двошарової перовськітоподібної структури $BaNd_2In_2O_7$ по типу $BaNd_{2-x}Sm_xIn_2O_7$: $0 \le x \le 1,8$. Методом Рітвельда визначена тетрагональна (просторова група $P4_2/mnm$) кристалічна структура фаз $BaNd_{2-x}Sm_xIn_2O_7$ зі ступенями заміщення атомів Nd рівними 0,5, 1,0, 1,5 і 1,8. Основою кристалічної структури $BaNd_{2-x}Sm_xIn_2O_7$ є двовимірні (нескінчені в площині *XY*) перовськітоподібні блоки, які складаються з двох шарів сполучених вершинами деформованих октаедрів InO_6. Атоми Ва локалізовані лише в позиції 4*f* всередині перовськітоподібного блоку, а атоми РЗЕ лише в позиції 8*j* на межі перовськітоподібних блоків. Сусідні перовськітоподібні блоки розділені шаром поліедрів LnO_9 та утримуюься разом міжблоковими зв`язками - O - Ln - O - . Встановлено, що ізовалентне заміщення атомів Nd на менші за розміром атоми Sm приводить до зменшення довжини міжблокової відстані Ln – O2 (з 0,230(2) нм до 0,206(2) нм) та до збільшення ступеня деформації міжблокових поліедрів LnO_9, внутрішньоблокових поліедрів BaO_{12} та октаедрів InO_6. Такі структурні зміни дестабілізують міжблокову «зшивку» і є одними із основних факторів руйнування шаруватої перовськітоподібної структури фаз $BaNd_{2-x}Sm_xIn_2O_7$ при $x > 1,8$. Одержані дані можуть бути використані для цілеспрямованого регулювання структурно залежних властивостей матеріалів на основі індату $BaNd_2In_2O_7$.

Ключові слова: сполуки типу $A_{n+1}B_nO_{3n+1}$, шарувата перовськітоподібна структура, рентгенівська порошкова дифрактометрія, ізоморфізм, тверді розчини.