Research Article

Yuri Titov, Nadezhda Belyavina, Mykola Slobodyanik, Olesya Nakonechna*,
Nataliia Strutynska, Mariana Tymoshenko

Effect of isovalent substitution on the crystal structure and properties of two-slab indates $\text{BaLa}_{2-x}\text{Sm}_x\text{In}_2\text{O}_7$

<https://doi.org/10.1515/chem-2020-0090>

received April 22, 2020; accepted September 02, 2020

Abstract: Exploring the effect of isomorphic substitution of atoms on crystal structure and features of oxide compounds is one of the main tasks of modern materials science. This paper deals with the La/Sm isovalent substitution in a two-slab perovskite-like $\text{BaLa}_2\text{In}_2\text{O}_7$ structure and its effect on the structural features and magnetic properties of $\text{BaLa}_{2-x}\text{Sm}_x\text{In}_2\text{O}_7$ indates synthesized. A complete characterization including data of scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDS), X-ray diffraction (XRD), structural calculations (Rietveld method), second optical harmonic generation of the laser radiation, calculations of valence bond sums (VBS), and magnetic susceptibility data of phases obtained is presented. The existence region of $\text{BaLa}_{2-x}\text{Sm}_x\text{In}_2\text{O}_7$ solid solutions with a two-slab perovskite-like structure ($0 \leq x \leq 1.8$) was established, and their coordinate parameters were refined. The character of barium and RE atoms distribution in $\text{BaLa}_{2-x}\text{Sm}_x\text{In}_2\text{O}_7$ structure has determined, and the correlation between substitution degree of lanthanum atoms and the length of Ln–O₂ interblock distance has revealed. The magnetic properties of $\text{BaLa}_{2-x}\text{Sm}_x\text{In}_2\text{O}_7$ were considered in terms of the crystal field effect.

Keywords: phases of $\text{A}_{n+1}\text{B}_n\text{O}_{3n+1}$ -type, slab perovskite-like structure, X-ray powder diffraction, magnetic susceptibility, functional oxide materials

* **Corresponding author: Olesya Nakonechna**, Department of Physics, Taras Shevchenko National University of Kyiv, 4 Glushkov Ave., 03022, Kyiv, Ukraine, e-mail: les@univ.kiev.ua, lesnak4@gmail.com, tel: +380-44-526-2367

Yuri Titov, Mykola Slobodyanik, Nataliia Strutynska, Mariana Tymoshenko: Department of Chemistry, Taras Shevchenko National University of Kyiv, 64/13, Volodymyrska Str., 01601, Kyiv, Ukraine
Nadezhda Belyavina: Department of Physics, Taras Shevchenko National University of Kyiv, 4 Glushkov Ave., 03022, Kyiv, Ukraine

1 Introduction

Compounds of $\text{A}_{n+1}\text{B}_n\text{O}_{3n+1}$ family (A = Sr, Ba, Ca, Ln, Na, K; B = Al, Ga, Fe, Ni, Cr, Sc, In, Ti, Sn, Zr, Hf, Pb, Mn; n is the amount of BO_6 octahedra slabs in a block, $n = 1-3$) with a slab perovskite-like structure (SPS) find a number of practically important electrophysical, optical, and catalytic properties [1–18]. In particular, representatives of this family of compounds may find an application as humidity sensor materials with high sensitivities and fast response time [3], as oxygen sensors and solid electrolytes in solid-state fuel cells, showing a high degree of flexibility in controlling electrical and transport properties [4,5]. Thus, $\text{Ba}_8\text{In}_6\text{O}_{17}$ (with $\text{A}_{n+1}\text{B}_n\text{O}_{3n+1}$ -type structure) exhibits high oxide ion conductivity comparable to stabilized zirconia, which is commercially used as a solid electrolyte [6]. Compounds of $\text{A}_{n+1}\text{B}_n\text{O}_{3n+1}$ exhibit photocatalytic activity of water decomposition into H_2 and O_2 under UV light [7,8] and luminescent parameters of the doped $\text{A}_{n+1}\text{B}_n\text{O}_{3n+1}$ compounds indicate the prospect of their use as matrices for lumiphore and laser materials [9–14]. However, it should be noted that, unlike the Mn-, Co- or Fe-containing $\text{A}_n\text{B}_n\text{O}_{3n+1}$ compounds [15–18], the magnetic properties of Sm-containing $\text{A}_{n+1}\text{B}_n\text{O}_{3n+1}$ compounds with SPS have not been studied yet.

It is known that isomorphic substitution A/B of atoms in the crystallographic positions is one of the common ways of controlling the characteristics of oxides and oxide-based materials [5,7,16,19,20]. Note that the effect of isomorphic substitution is well studied for Sr-containing $\text{A}_{n+1}\text{B}_n\text{O}_{3n+1}$ phases with $n = 1$ and $n = 2$ [21–26]. However, the composition/structure relationship in Ba-containing $\text{A}_{n+1}\text{B}_n\text{O}_{3n+1}$ phases with $n = 2$ was only defined for Ba/Sr substitution [27] in $\text{Ba}_{1-x}\text{Sr}_x\text{La}_2\text{In}_2\text{O}_7$ phases. At the same time, there is no data on the effect of isovalent substitution of RE atoms in $\text{BaLn}_2\text{In}_2\text{O}_7$ indates (Ln = La, Pr, Nd) on their structure and properties.

The aim of present research was to study the conditions of La/Sm isovalent substitution in a two-slab $\text{BaLa}_2\text{In}_2\text{O}_7$ SPS and to determine its effect on the structural features and magnetic properties of isovalently substituted $\text{BaLa}_{2-x}\text{Sm}_x\text{In}_2\text{O}_7$ indates synthesized. To completely characterize this system, the present paper includes a systematic study of conditions of polymorphous substitution, crystal structure, and magnetic properties of $\text{BaLa}_{2-x}\text{Sm}_x\text{In}_2\text{O}_7$ samples. The study of the $\text{Ln}/\text{Ln}^{\text{I}}$ substitution is a venture into the theory of the formation of Ba-containing $\text{A}_{n+1}\text{B}_n\text{O}_{3n+1}$ compounds with SPS and is of apparent interest for understanding the composition/structure/features correlation for other representatives of oxide compounds with perovskite structure.

2 Experimental details

2.1 Reagents

Chemically pure $\text{Ba}(\text{CH}_3\text{COO})_2$ (≥ 99 wt%) was purchased from Ostchem (Ukraine), and chemically pure La $(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (≥ 99 wt%), $\text{Sm}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (≥ 99 wt%), and $\text{In}(\text{NO}_3)_3 \cdot 4.5\text{H}_2\text{O}$ (≥ 99.9 wt%) were purchased from Rare Metals Plant (Novosibirsk, Russia) and used for the synthesis of $\text{BaLa}_{2-x}\text{Sm}_x\text{In}_2\text{O}_7$ samples.

2.2 Fabrication of $\text{BaLa}_{2-x}\text{Sm}_x\text{In}_2\text{O}_7$

Preparation of the initial charge of co-crystallized salts for the subsequent synthesis of $\text{BaLa}_{2-x}\text{Sm}_x\text{In}_2\text{O}_7$ polycrystalline indates was carried out by co-crystallization (evaporation at intensive mixing) of the mixture of barium acetate, lanthanum, samarium, and indium nitrates aqueous solution (the ratio is equal to $\text{Ba}:\text{La}:\text{Sm}:\text{In} = 1:2 - x:x:2$ (increment $x = 0.1$)) with further thermal treatment of the product obtained with a gas-jet to remove the main part of the nitrogen oxides. The powder obtained was ground and pressed (under pressure $p = 3 \times 10^8$ Pa) as the tablets with further heat treatment up to 1,570 K. Maximum heating temperature was reached in 2 h (heating rate didn't exceed 15 K/min), the cooling proceeded spontaneously together with the oven for 10 h. A two-stage (2 + 2 h) mode of tablet roasting at 1,570 K with intermediate grinding and repressing after the first stage was used. This procedure ensured the completeness of components interaction (according to XRD and SEM data).

2.3 Characterization

Morphology of the mechanically ground $\text{BaLa}_{2-x}\text{Sm}_x\text{In}_2\text{O}_7$ ceramic tablets was studied by the scanning electron microscopy technique (SEM, JEOL JAMP-9500F, Japan). JEOL JAMP-9500F is a field emission auger microprobe operated at 10 kV, which offers the flexibility of optional analysis functions such as energy-dispersive X-ray spectroscopy (EDS). EDS mappings of O, In, Ba, Sm, and La elements were performed on $15.3 \mu\text{m} \times 10.2 \mu\text{m}$ areas of as-prepared powder sample, which was placed on a carbon film and put into apparatus.

The X-ray powder diffraction data of the samples were collected with Shimadzu XRD-6000 diffractometer ($\text{CuK}\alpha$ radiation) in a discrete mode: the scanning interval 2θ was $(20-75)^\circ$, the step scan of 0.02° , counting time per step was 5 s. The peak positions and integrated intensities of the reflections observed were determined by full profile analysis.

To fulfill the preliminary data processing, as well as to carry out analysis and interpretation of the XRD data obtained, an original software package was applied, which includes a complete set of standard Rietveld procedures, namely, phase analysis of diffraction patterns using set of working base data, refinement of unit cell parameters, testing of the structure models proposed and crystal structure parameters refinement (including coordinates of atoms, atomic position filling, texture, etc.) [28].

Tests for generation of the second $I_{2\omega}$ were performed on polycrystalline samples using the Nd:YAG laser ($\lambda_\omega = 1.064 \mu\text{m}$ and $\lambda_{2\omega} = 0.532 \mu\text{m}$). The powder of four-slab $\text{La}_4\text{Ti}_4\text{O}_{14}$ ferroelectric was used as a standard material for estimating the non-centrosymmetric structure.

Temperature dependences of the magnetic susceptibility $\chi(T)$ of the indates synthesized were measured by the Faraday technique (using ABF-5 magnetometer) in a temperature range of 300–900 K in a purified argon atmosphere. To improve the quality of the experimental curve a set of magnetometric measurements was carried out for each sample, and the data obtained were averaged. An error of χ determination did not exceed 5%.

Ethical approval: The conducted research is not related to either human or animal use.

3 Results and discussion

SEM micrographs (Figure 1a) showed that mechanically dispersed $\text{BaLa}_{2-x}\text{Sm}_x\text{In}_2\text{O}_7$ ceramic consists of

irregularly shaped particles up to 10 μm in diameter with a smooth surface. Corresponding EDS maps showing the element's distribution have revealed the homogeneous composition of $\text{BaLa}_{2-x}\text{Sm}_x\text{In}_2\text{O}_7$ ($0 \leq x \leq 1.8$) particles (Figure 1b).

X-ray diffraction patterns of the heat-treated samples of co-crystallized salts have revealed the that existence range of $\text{BaLa}_{2-x}\text{Sm}_x\text{In}_2\text{O}_7$ phases with SPS is $0 \leq x \leq 1.8$ also. Powder diffraction data and the results of Rietveld refinement are shown in Figure 2. Their diffraction patterns are similar to those for the unsubstituted $\text{BaLa}_2\text{In}_2\text{O}_7$ compound [29] and are indexing well in the tetragonal system.

Destruction of two-slab $\text{BaLa}_{2-x}\text{Sm}_x\text{In}_2\text{O}_7$ indates with SPS takes place if the substitution degree x is higher than 1.8. Besides, if $x = 2$, this failure is accompanied by a formation of the two-phase system consisting of SmInO_3 with a perovskite-type structure and BaSmInO_4 indate with CaFe_2O_4 -type structure. It should be noted that B-positions of the BaSmInO_4 phase are occupied by Sm and In atoms simultaneously [30].

The lattice parameters (a and c values) of the tetragonal $\text{BaLa}_{2-x}\text{Sm}_x\text{In}_2\text{O}_7$ phases with SPS decrease monotonically within the existence range of the $\text{BaLa}_2\text{In}_2\text{O}_7$ -based solid solutions (Figure 3). Such dependence of the unit cell parameters is caused by the smaller size of the samarium atom and is typical for other solid solutions of the $\text{A}_{n+1}\text{B}_n\text{O}_{3n+1}$ compound with SPS [21–27].

Systematic extinction of the $\text{BaLa}_{2-x}\text{Sm}_x\text{In}_2\text{O}_7$ with SPS diffraction pattern indicates the following possible space groups: one centrosymmetric $P4_2/mnm$ and two noncentrosymmetric $P4_2nm$ or [31]. Results of the second optical harmonic generation of the laser radiation for

$\text{BaLa}_{2-x}\text{Sm}_x\text{In}_2\text{O}_7$ ($I_{2\omega}$) were compared $P\bar{4}n2d$ with those for the noncentrosymmetric $\text{La}_4\text{Ti}_4\text{O}_{14}$ phase with SPS ($I'_{2\omega}$) and showed that the relative intensity of signal does not exceed $0.01I'_{2\omega}$. According to ref. [32], insignificant $I_{2\omega}$ value unambiguously indicates that $\text{BaLa}_{2-x}\text{Sm}_x\text{In}_2\text{O}_7$ phases (as well as the initial $\text{BaLa}_2\text{In}_2\text{O}_7$ phase) belong to the centrosymmetric space group $P4_2/mnm$.

Taking into account the centrosymmetry of both $\text{BaLa}_{2-x}\text{Sm}_x\text{In}_2\text{O}_7$ indates ($0 < x \leq 1.8$) synthesized here and their prototype $\text{BaLa}_2\text{In}_2\text{O}_7$ indate [29], the atomic parameters of this indate-prototype were chosen as starting values for $\text{BaLa}_{2-x}\text{Sm}_x\text{In}_2\text{O}_7$ structures. Crystallographic data for $\text{BaLa}_2\text{In}_2\text{O}_7$ indate according to ref. [29] are as follows: $P4_2/mnm$ space group, $a = 0.5915(2)$ nm, $c = 2.086(1)$ nm, 4Ba atoms are placed in $4f\ x\ x\ 0$ with $x = 0.249$; 8La atoms are placed in $8j\ x\ x\ z$ with $x = 0.269$, $z = 0.185$; 8In atoms are placed in $8j\ x\ x\ z$ with $x = 0.260$, $z = 0.400$; 4O(1) atoms are placed in $4g\ x\ \bar{x}\ 0$ with $x = 0.806$; 8O(2) atoms are placed in $8j\ x\ x\ z$ with $x = 0.816$, $z = 0.290$; 8O(3) atoms are placed in $8h\ 0\ 0.5\ z$ with $z = 0.096$; 4O(4) atoms are placed in $4e\ 0\ 0\ z$ with $z = 0.126$; 4O(5) atoms are placed in $4e\ 0\ 0\ z$ with $z = 0.383$. Relevant structural calculations carried out using $\text{BaLa}_2\text{In}_2\text{O}_7$ as initial trial model led to a satisfactory agreement between the experimental and calculated intensities of reflections for each of the $\text{BaLa}_{2-x}\text{Sm}_x\text{In}_2\text{O}_7$ phases studied (the reliability factors R_B are about 0.04). Crystallographic data for the structures of several $\text{BaLa}_{2-x}\text{Sm}_x\text{In}_2\text{O}_7$ phases (with $x = 0.5, 1.0, 1.6$, and 1.8) obtained as a result of these calculations are listed in Table 1. Interatomic distances in each $\text{BaLa}_{2-x}\text{Sm}_x\text{In}_2\text{O}_7$ phase have been calculated based on the refined coordinate parameters of the atom. Moreover, a distortion degree (Δ) of the MeO_n polyhedra was calculated as

Figure 1: SEM micrographs of $\text{BaLa}_{0.5}\text{Sm}_{1.5}\text{In}_2\text{O}_7$ powder ceramic: $\times 1000$ (a); corresponding EDS maps showing the element's distribution (b).

Figure 2: Diffraction pattern (points), Rietveld refinement results (solid line) for $\text{BaLa}_{2-x}\text{Sm}_x\text{In}_2\text{O}_7$ with $x = 0, 0.5, 1.0, 1.8$ ($P4_2/mnm$) and diffraction pattern of "BaSm₂In₂O₇" ($\text{CuK}\alpha$ radiation).

Figure 3: Dependences of lattice parameters for $\text{BaLa}_{2-x}\text{Sm}_x\text{In}_2\text{O}_7$ phases on the degree of lanthanum atoms substitution (x).

$\Delta = 1/n \sum [(R_i - \bar{R})/\bar{R}]^2$ (where R_i is the Me–O distance, $\bar{R}$ is the Me–O average distance, n is the coordination number for Me atom) [33] (Table 2).

Unfortunately, it was impossible to determine correctly the localization of Ba, La, and Sm atoms in $\text{BaLa}_{2-x}\text{Sm}_x\text{In}_2\text{O}_7$ phases from XRD data due to the proximity of their atomic scattering factors. Therefore, the distribution of barium, lanthanum, and samarium atoms within the 4f and 8j crystallographic positions of the $\text{BaLa}_{2-x}\text{Sm}_x\text{In}_2\text{O}_7$ SPS structures was established by analyzing the valence bond sums (VBS) of these atoms in BaO_9 , BaO_{12} , $(\text{La}_{2-x}\text{Sm}_x)\text{O}_9$, and $(\text{La}_{2-x}\text{Sm}_x)\text{O}_{12}$ polyhedron (Table 3). Moreover, the Me–O bond valency (s) was calculated as $s = \exp((R_0 - R)/B)$ [34], where R_0 is the tabulated length of the monovalent bond, R is the experimental value of the bond length, and B is the tabulated value of the dispersion of the bond length,

which is equal to 0.037 nm and was applied to find R_0 . VBS was found from the valency of all bonds: $\text{VBS} = \sum s \cdot n$, where n is the number of bonds of this type. In the case of simultaneous filling of the position with lanthanum and samarium atoms, the above formula was applied to calculate VBS, while the standard value of R_0 was refined by the equation:

$$R_0 = R_0(\text{La}) \times K(\text{La}) + R_0(\text{Sm}) \times K(\text{Sm}),$$

where $R_0(\text{La})$ and $R_0(\text{Sm})$ are the tabulated lengths of the monovalent bond, $K(\text{La})$ and $K(\text{Sm})$ are the occupancy of this position. As can be seen from the data listed in Table 3, the VBS values of barium and RE atoms in the hypothetical BaO_9 and LnO_{12} polyhedron are significantly different from their chemical valences, while VBS values of these elements are much closer to their valences for the location of barium atoms in position 4f and RE atoms in position 8j.

Thus, the results of our calculations unambiguously indicate an ordered distribution of barium and RE atoms in $\text{BaLa}_{2-x}\text{Sm}_x\text{In}_2\text{O}_7$ phase with localization of barium atoms in the intrablock of cubo-octahedral voids of the perovskite-like block only and with localization of the RE atoms just in the LnO_9 polyhedron. Previously, such an atom arrangement was observed for unsubstituted $\text{BaLa}_2\text{In}_2\text{O}_7$ compound [29]. The likely reason for such character of distribution of barium and RE atoms in the $\text{BaLa}_{2-x}\text{Sm}_x\text{In}_2\text{O}_7$ of two-slab SPS is the tendency of relatively smaller RE atoms to occupy small MeO_9 polyhedra.

It was shown that the main structural units of the synthesized $\text{BaLa}_{2-x}\text{Sm}_x\text{In}_2\text{O}_7$ indiate with SPS are the directly unrelated two-dimensional (infinite in both X

Table 1: Crystal data for $\text{BaLa}_{2-x}\text{Sm}_x\text{In}_2\text{O}_7$ phases ($P4_2/mnm$ space group)

Atom	Site	$\text{BaLa}_{1.5}\text{Sm}_{0.5}\text{In}_2\text{O}_7$			$\text{BaLaSmIn}_2\text{O}_7$			$\text{BaLa}_{0.4}\text{Sm}_{1.6}\text{In}_2\text{O}_7$			$\text{BaLa}_{0.2}\text{Sm}_{1.8}\text{In}_2\text{O}_7$		
		Occ.	X	Z	Occ.	X	Z	Occ.	X	Z	Occ.	X	Z
Ba	4f	1	0.2520(2)	0	1	0.2540(3)	0	1	0.2540(2)	0	1	0.2540(3)	0
La	8j	0.75	0.2720(2)	0.1852(2)	0.5	0.2758(2)	0.1854(2)	0.2	0.2791(3)	0.1853(2)	0.1	0.2800(3)	0.1854(2)
Sm		0.25			0.5			0.8			0.9		
In	8j	1	0.2599(3)	0.3983(3)	1	0.2607(2)	0.3977(3)	1	0.2616(2)	0.3964(2)	1	0.2622(2)	0.3960(3)
O(1)	4g	1	0.806(2)	0	1	0.803(3)	0	1	0.790(2)	0	1	0.794(2)	0
O(2)	8j	1	0.816(2)	0.290(3)	1	0.813(2)	0.289(3)	1	0.803(2)	0.286(2)	1	0.803(3)	0.285(2)
O(3)	8h	1	0	0.096(2)	1	0	0.095(2)	1	0	0.098(2)	1	0	0.098(2)
O(4)	4e	1	0	0.130(2)	1	0	0.135(2)	1	0	0.145(3)	1	0	0.144(2)
O(5)	4e	1	0	0.383(3)	1	0	0.390(3)	1	0	0.395(2)	1	0	0.400(3)
Lattice parameters, a, c , nm		0.59129(3); 2.0732(1)			0.59028(5); 2.0614(2)			0.5888(1); 2.0413(1)			0.5883(1); 2.0358(1)		
Total isotropic B factor, nm^2		$0.69(4) \times 10^{-2}$			$0.48(4) \times 10^{-2}$			$0.12(5) \times 10^{-2}$			$0.11(6) \times 10^{-2}$		
Reliability factor, R_B		0.04			0.039			0.047			0.037		

Table 2: Selected interatomic distance (*d*) and degree of distortion (Δ) of MeO_n polyhedra in the crystal structure of BaLa₂In₂O₇ compound and BaLa_{2-x}Sm_xIn₂O₇ phases

Atom-atom	BaLa _{2-x} Sm _x In ₂ O ₇				
	<i>x</i> = 0 [29] <i>d</i> , nm	<i>x</i> = 0.5 <i>d</i> , nm	<i>x</i> = 1 <i>d</i> , nm	<i>x</i> = 1.6 <i>d</i> , nm	<i>x</i> = 1.8 <i>d</i> , nm
Polyhedron BaO₁₂					
Ba-2 O(1)	0.264(2)	0.266(1)	0.268(1)	0.274(1)	0.272(2)
Ba-4 O(3)	0.290(1)	0.289(1)	0.286(1)	0.289(1)	0.288(1)
Ba-2 O(5)	0.322(2)	0.319(2)	0.306(1)	0.297(2)	0.289(1)
Ba-2 O(1)	0.331(1)	0.329(1)	0.326(2)	0.317(2)	0.319(1)
Ba-2 O(4)	0.335(1)	0.342(2)	0.350(2)	0.364(1)	0.361(2)
Ba-O _{av.}	0.305	0.305	0.304	0.305	0.303
Δ	72×10^{-4}	74×10^{-4}	82×10^{-4}	93×10^{-4}	95×10^{-4}
Polyhedron LnO₉					
Ln-1 O(2)*	0.230(2)	0.229(1)	0.226(1)	0.217(2)	0.214(1)
Ln-1 O(5)	0.240(1)	0.237(2)	0.243(2)	0.246(1)	0.252(2)
Ln-2 O(2)	0.252(2)	0.250(1)	0.249(1)	0.253(2)	0.253(2)
Ln-1 O(4)	0.257(1)	0.255(1)	0.253(1)	0.247(1)	0.248(1)
Ln-2 O(3)	0.281(2)	0.280(2)	0.281(2)	0.275(2)	0.275(2)
Ln-2 O(2)	0.351(1)	0.352(2)	0.352(2)	0.348(1)	0.349(1)
Ln-O _{av.}	0.277	0.276	0.276	0.274	0.274
Δ	234×10^{-4}	249×10^{-4}	250×10^{-4}	246×10^{-4}	250×10^{-4}
Polyhedron InO₆					
In-1 O(4)	0.209(1)	0.209(1)	0.211(2)	0.216(2)	0.214(1)
In-2 O(3)	0.209(2)	0.210(2)	0.209(1)	0.209(1)	0.209(1)
In-1 O(1)	0.212(1)	0.214(1)	0.214(1)	0.213(1)	0.213(1)
In-1 O(5)	0.220(2)	0.220(2)	0.218(1)	0.218(2)	0.218(2)
In-1 O(2)	0.238(1)	0.233(2)	0.232(2)	0.232(1)	0.232(2)
In-O _{av.}	0.216	0.216	0.216	0.216	0.216
Δ	24×10^{-4}	15×10^{-4}	14×10^{-4}	13×10^{-4}	13×10^{-4}

* – intrablock distance (O(2) atom is placed in the neighbor perovskite-like block).

and *Y* axes) perovskite-like blocks, each of which consists of two slabs connected by vertices of the deformed InO₆ octahedra (Figure 4a). Adjacent blocks are shifted by a half of the perovskite cube edge and alternate with each other in a direction of the *XY* plane diagonal. Neighboring perovskite-like blocks are separated by a slab of LnO₉ polyhedra and are held together by means of interblock bonds –O–Ln–O.

Eight oxygen atoms (four O(2), two O(3), one O(4), and one O(5)) of the LnO₉ polyhedron belong to the same block as Ln atoms, while the ninth oxygen atom (O(2)) refers to the neighboring block (Figure 4b). This Ln–O(2) interblock bond is the shortest (0.230(2)–0.214(1) nm) among all the bonds of LnO₉ polyhedron (Table 2). Moreover, its length approaches the minimum known for the (La,Sm)–O distances. This confirms a conclusion made on the base of VBS data on the impossibility of arrangement barium atoms, which are much larger than lanthanum and samarium atoms, in the 8j position in the MeO₉ polyhedron between perovskite-like blocks. It also indicates Ba atom

localization in 4f position in intrablock voids of the perovskite-like block only, where its coordination polyhedron is a deformed BaO₁₂ cuboctahedron. It should be noted that the two O(2) atoms are located at significantly higher distances (0.352(2)–0.348(1) nm) from the RE atom among nine oxygen atoms of the LnO₉ polyhedron (Table 2); therefore, the coordination number of RE atoms could be considered as 7 + 2.

Analysis of the (La,Sm)–O(2) interblock bond length in BaLa_{2-x}Sm_xIn₂O₇ SPS indicates that the replacement of lanthanum atoms by smaller samarium atoms leads to a significant decrease in the length of the (La,Sm)–O(2) interblock bond (from 0.230(2) nm to 0.214(1) nm) (Figure 5 and Table 2). This approaches the structure of BaLa_{2-x}Sm_xIn₂O₇ indate to the structure of three-dimensional perovskite, and it is one of the main restrictive factors for these phases' existence region and the absence of BaSm₂In₂O₇ compound.

An increase in the number of small samarium atoms in the (La,Sm)O₉ interblock polyhedra affects the structure of

Table 3: Valence bonds sum (VBS) calculated for Ba and Ln atoms in the MeO_n polyhedra of $\text{BaLa}_{2-x}\text{Sm}_x\text{In}_2\text{O}_7$ with SPS

x	$R_0 (\text{La}_{2-x}\text{Sm}_x)$, nm	VBS			
		Site 4f		Site 8j	
		Polyhedron		Polyhedron	
		BaO_{12}	LnO_{12}	BaO_9	LnO_9
0 [29]	0.2172	1.92	1.42	3.77	2.78
0.5	0.2151	1.90	1.32	3.96	2.75
1.0	0.213	2.00	1.31	3.97	2.61
1.5	0.21258	2.05	1.34	3.94	2.57
1.1	0.21195	2.10	1.34	4.00	2.56
1.25	0.21176	1.94	1.23	4.17	2.65
1.5	0.2109	1.91	1.19	4.25	2.64
1.6	0.21048	1.91	1.18	4.27	2.63
1.8	0.20964	2.04	1.22	4.3	2.57
R_0 , nm		Bond [34]			
0.2285		Ba–O			
0.2172		La–O			
0.2088		Sm–O			

perovskite-like block with SPS also. In particular, it slightly increases the deformation of the BaO_{12} intra-block polyhedra (Table 2).

It should be noted that the structure features of SPS revealed here for the $\text{BaLa}_{2-x}\text{Sm}_x\text{In}_2\text{O}_7$ phases are similar to those for the unsubstituted $\text{BaLn}_2\text{In}_2\text{O}_7$ ($\text{Ln} = \text{La}, \text{Pr}, \text{Nd}$). In particular, a decrease in the crystalline ionic radius of RE atoms in $\text{BaLn}_2\text{In}_2\text{O}_7$ indicates results in a gradual decrease of the $\text{Ln}-\text{O}(2)$ interblock bond length [29].

To study the effect of $\text{La}^{3+}/\text{Sm}^{3+}$ substitution on magnetic properties of $\text{BaLa}_{2-x}\text{Sm}_x\text{In}_2\text{O}_7$ with SPS, we analyzed the temperature dependences of magnetic susceptibility $\chi(T)$ for samples with $x = 1$ and $x = 1.8$ (Figure 6).

Figure 4: Crystal structure of $\text{BaLaSmIn}_2\text{O}_7$ as an arrangement of InO_6 octahedra and Ba (black circles) and La, Sm atoms (gray circles) (a); interblock boundary pattern for $\text{BaLa}_{0.2}\text{Sm}_{1.8}\text{In}_2\text{O}_7$ (La, Sm) atoms – gray circles) (b). **Figure 5:** Dependence of $\text{Ln}-\text{O}$ interblock distance (d) in LnO_9 external block polyhedra on the substitution of La atoms in $\text{BaLa}_{2-x}\text{Sm}_x\text{In}_2\text{O}_7$ phases with SPS.

The $\chi(T)$ curves exhibited a moderately weak temperature dependence in temperature range (300–600) K, suggesting the presence of Van Vleck paramagnetism as usually observed for Sm^{3+} oxides [35–40]. The electronic configuration of Sm^{3+} ($4f^5$), which has the ground J -multiplet ($J = 5/2$), on the site symmetry of C_{2v} indicates the ground state is a Kramers doublet [35]. For fitting the χ vs T curve at higher temperatures (up to 600 K), we thus used the Curie–Weiss law accompanied by a temperature-independent term χ_{const} is given as follows:

$$\chi(T) = \chi_{\text{const}} + \frac{C}{T - \theta},$$

where C is the Curie constant and θ is the Curie temperature [35].

Besides, the $\chi(T)$ curves presented in Figure 6 clearly demonstrate a change in magnetic characteristics of the phases studied. In particular, one can see a change of $\chi(T)$ slope at 630, 770, and 810 K (Figure 6a). Processing the obtained $\chi(T)$ curves in $(\chi \cdot T; T)$ coordinates (Figure 6b)

Figure 6: Temperature dependences of the magnetic susceptibility of $\text{BaLa}_{2-x}\text{Sm}_x\text{In}_2\text{O}_7$.

and $(\chi^{-1}; T)$ (Figure 6c) reveals linear dependences of $(\chi \cdot T)$ (T) curve in the temperature range 300–630 K, while $\chi^{-1}(T)$ curve demonstrates linear sections at higher temperatures.

The effective magnetic moments per samarium atom μ_{eff} were calculated taking into account the experimentally obtained C values, which are unchanged within a certain temperature range. The values calculated are listed in Table 4 and are much smaller ($0.35\text{--}0.56 \mu_B$) than the free-ion value of $0.83 \mu_B$, indicating that the Sm magnetic moment is under the influence of crystal electric field (CEF) of the perovskite structure. Note that a small μ_{eff} was often observed for Sm^{3+} oxides such as $0.44 \mu_B$ for $\text{KBaSm}(\text{BO}_3)_2$ [39], $0.53 \mu_B$ for $\text{Sm}_3\text{Sb}_3\text{Mg}_2\text{O}_{14}$ [38], $0.53 \mu_B$ for $\text{Sm}_2\text{Zr}_2\text{O}_7$ [40], and $0.15 \mu_B$ for $\text{Sm}_2\text{Ti}_2\text{O}_7$ [40]. The negative θ (Table 4) may indicate that the dominant magnetic interaction is antiferromagnetic even though it is very small and has to be interpreted carefully with the presence of CEF effects.

The data obtained allow us to speculate about the crystal field effects in the $\text{BaLa}_{2-x}\text{Sm}_x\text{In}_2\text{O}_7$ indates. It was shown that the temperature increase leads to a change in the effective magnetic moment of the Sm^{3+} ion, as it is listed in Table 4. In our opinion, such alternation of the μ_{eff} magnetic moment may indicate not only the rearrangement of magnetic sublattices of the solid solution studied but also the prerequisite to the existence of polymorphic structural transformation of the phases close by structure [35,37].

4 Conclusions

In this work, the effect of isovalent substitution of lanthanum by samarium atoms in $\text{BaIn}_2\text{In}_2\text{O}_7$ indate with the formation of $\text{BaLa}_{2-x}\text{Sm}_x\text{In}_2\text{O}_7$ solid solution ($0 \leq x \leq 1.8$) and features of this SPS are defined. The ordered distribution of barium and REM atoms in $\text{BaLa}_{2-x}\text{Sm}_x\text{In}_2\text{O}_7$ SPS has been revealed. It has been shown that the isovalent substitution degree increasing

Table 4: Effective magnetic moment and parameter θ of Sm^{3+} ion in $\text{BaLa}_{2-x}\text{Sm}_x\text{In}_2\text{O}_7$ phase

Temperature range (K)	$x = 1$		$x = 1.8$	
	$\mu_{\text{eff}} (\mu_B)$	θ (K)	$\mu_{\text{eff}} (\mu_B)$	θ (K)
300–630	0.35	—	0.46	—
630–770	0.56	–440	0.55	–440
810–900	0.35	–720	0.44	–650

leads to the convergence of two perovskite-like slabs of InO_6 octahedra connected by vertices. This feature rearranges the two-slab perovskite-like structure of $\text{BaLa}_{2-x}\text{Sm}_x\text{In}_2\text{O}_7$ indates to the structure of three-dimensional perovskite and is one of the main factors limiting their existence field. The magnetism of these compounds is understood by the localized 4f electrons of Sm^{3+} . $\text{BaLa}_{2-x}\text{Sm}_x\text{In}_2\text{O}_7$ showed the reduced magnetic moment because of the crystal field effect and strong Van Vleck paramagnetism.

Analysis of the data obtained made it possible to establish the relationship between the composition, structure, and magnetic characteristics of the $\text{BaLa}_{2-x}\text{Sm}_x\text{In}_2\text{O}_7$ phases. All this information creates a background for the control of $\text{BaLa}_{2-x}\text{Sm}_x\text{In}_2\text{O}_7$ structural characteristics by consequent isovalent substitution of atoms in A position of SPS.

Conflict of interest: Authors declare no conflict of interest.

References

- [1] Aleksandrov KS, Beznosikov BV. Perovskites. Present and Future. Novosibirsk: RAS; 2004. (in Russian).
- [2] Schaak RE, Mallouk TE. Perovskites by design: A toolbox of solid-state reactions. Chem Mater. 2002;14(4):1455–71. doi: 10.1021/cm010689m.
- [3] Kim IS, Nakamura T, Itoh M. Humidity sensing effects of the layered oxides $\text{SrO} \cdot (\text{LaScO}_3)_n$ ($n = 1, 2, \infty$). J Cer Soc Jpn. 1993;101(7):800–3. doi: 10.2109/jcersj.101.800.
- [4] Navas C, Loe HC. Conductivity studies on oxygen-deficient Ruddlesden–Popper phases. Solid State Ion. 1996;93(1–2):171–6. doi: 10.1016/S0167-2738(96)00515-2.
- [5] Kato S, Ogasawara M, Sugai M, Nakata S. Synthesis and oxide ion conductivity of new layered perovskite $\text{La}_{1-x}\text{Sr}_{1+x}\text{InO}_{4-d}$. Solid State Ion. 2002;149(1–2):53–7. doi: 10.1016/S0167-2738(02)00138-8.
- [6] Zhen YS, Goodenough JB. Oxygen-ion conductivity in $\text{Ba}_8\text{In}_6\text{O}_{17}$. Mater Res Bull. 1990;25(6):785–90. doi: 10.1016/0025-5408(90)90207-I.

- [7] Kim HG, Becker OS, Jang JS, Ji SM, Borse PH, Lee JS. A generic method of visible light sensitization for perovskite-related layered oxides: Substitution effect of lead. *J Sol St Chem.* 2006;179:1214–8. doi: 10.1016/j.jssc.2006.01.024.
- [8] Shimizu K, Itoh S, Hatamachi T, Kodama T, Sato M, Toda K. Photocatalytic water splitting on Ni-intercalated Ruddlesden–Popper tantalate $\text{H}_2\text{La}_{2/3}\text{Ta}_2\text{O}_7$. *Chem Mater.* 2005;17(20):5161–6. doi: 10.1021/cm050982c.
- [9] Kamimura S, Yamada H, Xu C-N. Strong reddish-orange light emission from stress-activated $\text{Sr}_{n+1}\text{Sn}_n\text{O}_{3n+1}:\text{Sm}^{3+}$ ($n = 1, 2$) with perovskite-related structures. *Appl Phys Lett.* 2012;101(9):91–113. doi: 10.1063/1.4749807.
- [10] Yu T, Nedilko SG, Chornii V, Scherbatskii V, Belyavina N, Markiv V, et al. Crystal structure and luminescence of layered perovskites $\text{Sr}_3\text{LnInSnO}_8$. *Solid State Phenom.* 2015;230:67–72. doi: 10.4028/www.scientific.net/SSP.230.67.
- [11] Ueda K, Yamashita T, Nakayashiki K, Goto K, Maeda T, Furui K, et al. Green, orange, and magenta luminescence in strontium stannates with perovskite-related structures. *Jap J Appl Phys.* 2006;45(9A):6981–3. doi: 10.1143/JJAP.45.6981.
- [12] Yang HM, Shi JX, Gong ML. A new luminescent material, $\text{Sr}_2\text{SnO}_4:\text{Eu}^{3+}$. *J Alloy Comp.* 2006;415(1–2):213–5. doi: 10.1016/j.jallcom.2005.04.221.
- [13] Chau PTM, Ryu KH, Yo CH. Influence of the technological conditions on the luminescence of Eu^{3+} ions in Sr_2SnO_4 . *J Mater Sci.* 1998;33(5):1299–302. doi: 10.1023/A:1004350314959.
- [14] Cockroft NJ, Lee SH, Wright JC. Site-selective spectroscopy of defect chemistry in SrTiO_3 , Sr_2TiO_4 , and $\text{Sr}_3\text{Ti}_2\text{O}_7$. *Phys Rev B.* 1991;44(9):4117–26. doi: 10.1103/PhysRevB.44.4117.
- [15] Lobanov MV, Greenblatt M, Caspi EN, Jorgensen JD, Sheptyakov DV, Toby BH. Crystal and magnetic structure of the $\text{Ca}_3\text{Mn}_2\text{O}_7$ Ruddlesden–Popper phase: Neutron and synchrotron X-ray diffraction study. *J Phys: Condens Matter.* 2004;16(29):5339–48. doi: 10.1088/0953-8984/16/29/023.
- [16] Fawcett ID, Veith GM, Greenblatt M, Croft M, Nowik I. Properties of the $n = 3$ Ruddlesden + Popper Phases $\text{Sr}_4\text{Mn}_{3-x}\text{Fe}_x\text{O}_{10-\delta}$ ($x = 1, 1.5, 2$). *J Solid State Chem.* 2000;155(1):96–104. doi: 10.1006/jssc.2000.8904.
- [17] Battle PD, Burley JC, Gallon DJ, Grey CP, Sloan J. Magnetism and structural chemistry of the $n = 2$ Ruddlesden–Popper phase $\text{La}_3\text{LiMnO}_7$. *J Solid State Chem.* 2004;177(1):119–25. doi: 10.1016/S0022-4596(03)00333-5.
- [18] Hansteen OH, Fjellvag H, Hauback BC. Crystal structure, thermal and magnetic properties of $\text{La}_4\text{Co}_3\text{O}_9$. Phase relations for $\text{La}_4\text{Co}_3\text{O}_{10-\delta}$ ($0.00 \leq \delta \leq 1.00$) at 673 K. *J Mater Chem.* 1998;8(9):2089–93. doi: 10.1039/A801798K.
- [19] Bianco A, Cacciotti I, Lamastra FR. Eu-doped titania nanofibers: Processing, thermal behaviour and luminescent properties. *J Nanosci Nanotechnol.* 2010;10(8):5183–90. doi: 10.1166/jnn.2010.2215.
- [20] Cacciotti I, Bianco A, Pezzotti G, Gusmano G. Terbium and Ytterbium-doped titania luminescent nanofibers by means of electrospinning technique. *Mater Chem Phys.* 2011;126(3):532–41. doi: 10.1016/j.matchemphys.2011.01.034.
- [21] Titov YA, Belyavina NM, Slobodyanik MS, Nakonechna OI, Strutynska NY. Effect of size factor on the Ruddlesden–Popper single-slab compounds structure features. *French-Ukrainian J Chem.* 2019;7(1):10–15. doi: 10.17721/fujcV7I1P10-15.
- [22] Titov YA, Belyavina NM, Slobodyanik MS, Chumak VV, Timoshenko MV, Tomazenko LV. Synthesis and structural features of slab structure $\text{SrLa}_{1-x}\text{Sm}_x\text{InO}_4$. *Dopov Nac akad Nauk Ukr.* 2019;1:72–8. doi: 10.15407/dopovidi2019.01.072.
- [23] Titov YA, Belyavina NM, Slobodyanik MS, Chumak VV, Nakonechna OI. Effect of composition on the $\text{SrNdSc}_{1-x}\text{In}_x\text{O}_4$ slab structure. *Voprosy Khimii i Khimicheskoi Tekhnologii.* 2019;3:53–8. doi: 10.32434/0321-4095-2019-124-3-53-58.
- [24] Titov YA, Belyavina NM, Slobodyanik MS, Chumak VV, Nakonechna OI. Synthesis and crystal structure of isovalently substituted slab $\text{SrLa}_{2-x}\text{Dy}_x\text{Sc}_2\text{O}_7$ scandates. *Voprosy Khimii i Khimicheskoi Tekhnologii.* 2019;6:228–35. doi: 10.32434/0321-4095-2019-127-6-228-235.
- [25] Titov YA, Belyavina NM, Slobodyanik MS, Chumak VV, Nakonechna OI. Effect of isovalent substitution of lanthanum atoms on the slab structure of indates $\text{SrLa}_{1-x}\text{Nd}_x\text{InO}_4$. *Voprosy Khimii i Khimicheskoi Tekhnologii.* 2019;1:67–72. doi: 10.32434/0321-4095-2019-122-1-67-72.
- [26] Titov YA, Belyavina NM, Slobodyanik MS, Chumak VV, Nakonechna OI. Features of the $\text{SrLa}_2\text{Sc}_{2-x}\text{In}_x\text{O}_7$ two-slab structure. *Voprosy Khimii i Khimicheskoi Tekhnologii.* 2020;2:118–24. doi: 10.32434/0321-4095-2020-129-2-118-124.
- [27] Titov YA, Belyavina NM, Slobodyanik MS, Chumak VV. Crystal structure of isovalent substituted layered indates $\text{Ba}_{1-x}\text{Sr}_x\text{La}_2\text{In}_2\text{O}_7$. *Dopov Nac akad Nauk Ukr.* 2016;6:95–102. doi: 10.15407/dopovidi2016.06.095.
- [28] Dashevskiy M, Boshko O, Nakonechna O, Belyavina N. Phase transformations at mechanical milling of the equiatomic Y-Cu powder mixture. *Mettallofizika Noveishie Tekhnologii.* 2017;39(4):541–52. doi: 10.15407/mfint.39.04.0541.
- [29] Titov YA, Belyavina NM, Markiv VY, Slobodyanik MS, Kraevska YA, Yaschuk VP. Synthesis and crystal structure of $\text{BaLn}_2\text{In}_2\text{O}_7$. *Dopov Nac akad Nauk Ukr.* 2010;1:148–154. <http://dspace.nbuv.gov.ua/handle/123456789/19268>.
- [30] Titov YA, Belyavina NM, Markiv VY, Slobodyanik MS, Krayevska YA. Synthesis and crystal structure of BaLaInO_4 and SrLnInO_4 ($\text{Ln} = \text{La, Pr}$). *Dopov Nac akad Nauk Ukr.* 2009;10:160–6.
- [31] Hanh T. International tables for crystallography. Space Group Symmetry. Vol. A. Dordrecht: Springer; 2005.
- [32] Dougherty JP, Kurtz SK. A second harmonic analyzer for the detection of non-centrosymmetry. *J Appl Crystallogr.* 1976;9(2):145–58. doi: 10.1107/S0021889876010789.
- [33] Shannon RD. Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides. *Acta Crystallogr A.* 1976;32:751–67. doi: 10.1107/S0567739476001551.
- [34] Brown ID, Altermatt D. Bond-valence parameters obtained from a systematic analysis of the inorganic crystal structure database. *Acta Crystallogr B.* 1985;41(4):244–7. doi: 10.1107/S0108768185002063.
- [35] Wohlfarth EP, editor. Handbook of Magnetic Materials. Vol. 1, North-Holland Publishing Company; 1980.
- [36] Ozawa TC, Taniguchi T, Kawaji Y, Mizusaki S, Nagata Y, Noro Y, et al. Magnetization and specific heat measurement of the Shastry–Sutherland lattice compounds: $\text{Ln}_2\text{BaPdO}_5$ ($\text{Ln} = \text{La, Pr, Nd, Sm, Eu, Gd, Dy, Ho}$). *J Alloy Compd.* 2008;448(1):96–103. doi: 10.1016/j.jallcom.2007.05.036.

- [37] Goya GF, Mercader RC, Causa MT, Tovar M. Magnetic properties of $\text{Pnma-}R_2\text{BaZnO}_5$ oxides ($R = \text{Sm, Eu, Dy and Ho}$). *J Phys Condens Matter*. 1996;8(44):8607–12. doi: 10.1088/0953-8984/8/44/012.
- [38] Sanders MB, Baroudi KM, Krizan JW, Mukadam OA, Cava RJ. Synthesis, crystal structure, and magnetic properties of novel 2D kagome materials $\text{RE}_3\text{Sb}_3\text{Mg}_2\text{O}_{14}$ ($\text{RE} = \text{La, Pr, Sm, Eu, Tb, Ho}$): Comparison to $\text{RE}_3\text{Sb}_3\text{Zn}_2\text{O}_{14}$ family. *Phys Status Solidi (b)*. 2016;253(10):2056–65. doi: 10.1002/pssb.201600256.
- [39] Sanders MB, Cevallos FA, Cava RJ. Magnetism in the $\text{KBaRE}(\text{BO}_3)_2$ ($\text{RE} = \text{Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu}$) series: Materials with a triangular rare earth lattice. *Mater Res Express*. 2017;4(3):036102. doi: 10.1088/2053-1591/aa60a2.
- [40] Singh S, Saha S, Dhar SK, Suryanarayanan R, Sood AK, Revcolevschi A. Manifestation of geometric frustration on magnetic and thermodynamic properties of the pyrochlores $\text{Sm}_2\text{X}_2\text{O}_7$ ($\text{X} = \text{Ti, Zr}$). *Phys Rev B*. 2008;77(5):054408. doi: 10.1103/PhysRevB.77.054408.