PHYSICS AND CHEMISTRY
OF SOLID STATE
V. 24, No. 4 (2023) pp. 742-747

Section: Chemistry

DOI: 10.15330/pcss.24.4.742-747

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Т. 24, № 4 (2023) С. 742-747

Хімічні науки

PACS: 546.43`65`631`682 ISSN 1729-4428

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Effect of scandium atoms substitution on the two-slab structure of scandate $BaGd_2Sc_2O_7$

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Tetragonal crystal structure (space group $P4_2/mnm$ (No 136)) of the isovalently substituted $BaGd_2Sc_{2-x}In_xO_7$ phase with $x = 0.5$ was determined by X-ray powder diffraction methods. The crystal structure of $BaGd_2Sc_{1.5}In_{0.5}O_7$ consists of two-dimensional perovskite-like blocks with a thickness of two slabs of $(Sc,In)O_6$ octahedra connected by vertices. A slab of GdO_9 polyhedra is located between the blocks. There are no direct (Sc,In) – O – (Sc,In) connections between the octahedra of adjacent blocks. They are "stitched" to each other with the help of – O – Gd – O – bonds. Ba atoms are arranged only in the cubooctahedral voids of the perovskite-like block and their coordination number is 12. Analysis of the crystal chemical characteristics of $BaGd_2Sc_2O_7$ and $BaGd_2Sc_{1.5}In_{0.5}O_7$ showed that upon the isovalent substitution of Sc atoms by large In atoms in slab perovskite-like structure leads to increase of the deformation degree of $(Sc,In)O_6$ octahedra, GdO_9 interblock polyhedra, increase in average (Sc,In) – O bond length and a decrease the degree deformation of BaO_{12} cuboctahedrons. Such changes lead to the destabilization of the slab perovskite-like structure and determine the limitation of the area of $BaGd_2Sc_{2-x}In_xO_7$ solid solutions and the absence of $BaGd_2In_2O_7$ compound.

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

Received 05 September 2023; Accepted 19 December 2023.

Introduction

The presence of complex of structurally sensitive properties in compounds of the $A_{n+1}B_nO_{3n+1}$ family (A = Ba, Sr, Ca, Ln, Na, K; B = Al, Ga, Fe, Ni, Cr, Sc, In, Ti, Sn, Zr, Hf, Pb, Mn; n is the number of BO_6 octahedra in the perovskite-like block (n = 1-3)), due to the features of their slab perovskite-like structure (SPS) [1-6], makes relevant and important the study of isomorphic substitutions impact on the structure and characteristics of phases on their basis.

Ceramic oxide materials with oxygen-ion conductivity, which include pure oxygen-ion conductors and mixed oxygen-ion and electronic or hole conductors attract considerable attention because of their potential application for oxygen membranes, oxygen sensors and solid oxide fuel cells.

The oxygen ion conductivity was found in indates and scandates of $A_{n+1}B_nO_{3n+1}$ type (A = Sr, Ba, Ln, B = Sc, In) with a single- slab (n = 1) SPS and was studied in detail in [7-11]. Since the oxygen-ion conductivity is strongly dependent on crystal structure, the synthesis and definition of the structure features of novel isomorphically substituted scandates and indates of $A_{n+1}B_nO_{3n+1}$ type with two-slab (n = 2) SPS seems to be a relevant and important scientific task.

In previous works the effect of isovalent substitution of atoms in single- and two-slab strontium-containing scandates $Sr_{0.7}Ca_{0.3}LaScO_4$ [12], $SrLa_{1-x}Gd_xScO_4$ [13], $Sr_{1-x}Ca_xLa_2Sc_2O_7$ [14], $SrLa_{2-x}Dy_xSc_2O_7$ [15],

$SrLa_2Sc_{2-x}In_xO_7$ [16] and in two-slab barium-containing scandate $BaLa_{2-x}Dy_xSc_2O_7$ [17] on the structure of their SPS were established. However, studies of the effect of Sc atoms substitution on the structure of two-slab SPS of $BaLn_2Sc_2O_7$ scandates have not been carried out yet.

The aim of this work was to study the effect of Sc atoms substitution with bigger In atoms on the structure of the original two-slab $BaLn_2Sc_2O_7$ scandates (Ln = La – Gd), in particular, the extreme member of this series with the greatest degree of SPS deformation – $BaGd_2Sc_2O_7$ [18]. The $BaGd_2Sc_{1.5}In_{0.5}O_7$ phase with a composition close to the maximum substitution limit of Sc atoms in the SPS of samples of the $BaGd_2Sc_{2-x}In_xO_7$ system ($x = 0.6 \div 0.7$) [19] was selected as the object of the study.

I. Materials and methods

The synthesis of $BaGd_2Sc_{1.5}In_{0.5}O_7$ was carried out by simultaneous crystallization (evaporation with intensive stirring) of a mixture of aqueous solutions of Ba acetate, nitrates of Gd, Sc and In with the ratio
Ba : Gd : Sc : In = 1 : 2 : 1.5 : 0.5 with subsequent heat treatment of the obtained product on a gas burner to remove the main mass of nitrogen oxides. The charge obtained in this way was grinded, pressed in the form of discs and subjected to successive three-stage (with grinding and re-pressing of the samples after each stage of heat treatment) annealing at 1173 K (5 hours) and 1573 K (2 hours + 2 hours). Chemically pure Ba acetate and Gd, Sc, and In nitrates were used as raw materials.

X-ray diffraction spectra of polycrystalline samples were collected on Shimadzu XRD-6000 diffractometer in a discrete mode (scan step 0.02°, point exposure 7 seconds, angle interval $2\theta = 19 - 68^0$) on copper filtered (arc graphite monochromator in front of the counter) CuK_α radation. The crystal structure of the samples obtained was determined by the Rietveld method. Primary processing of diffraction spectra and structural calculations were performed using the software complex, as described in [20].

Signal intensity of the second optical harmonic $I2_\omega$ of laser radiation was measured on polycrystalline samples according to the procedure described in Ref. [21] using a Nd:YAG laser in Q-modulation mode (peak power density of laser radiation at wavelength
λ_ω = 1064 nm 20 MW/cm^2, pulse duration 15 nanoseconds, beam cross-sectional area 0.9 mm^2).

II. Experimental results

The diffraction pattern of $BaGd_2Sc_{1.5}In_{0.5}O_7$ (Fig. 1) is similar to that of two-slab $BaGd_2Sc_2O_7$ ($P4_2$/mnm) [18]. Its indexing have revealed that $BaGd_2Sc_{1.5}In_{0.5}O_7$ SPS belongs to the tetragonal syngony. Systematics of extinction of reflections on the $BaGd_2Sc_{1.5}In_{0.5}O_7$ diffraction pattern corresponds to the following possible space groups: centrosymmetric $P4_2/mnm$ and non-centrosymmetric $P4_2nm$ or $P\bar{4}n_2$.

Signal generation of the second optical harmonic of laser radiation showed that $I_{2\omega}$ for $BaGd_2Sc_{1.5}In_{0.5}O_7$ has the same order as for centrosymmetric unsubstituted $BaGd_2Sc_2O_7$. This provides the basis for an unambiguous conclusion that the crystal structure of $BaGd_2Sc_{1.5}In_{0.5}O_7$ phases belongs to the centrosymmetric space group of $P4_2/mnm$.

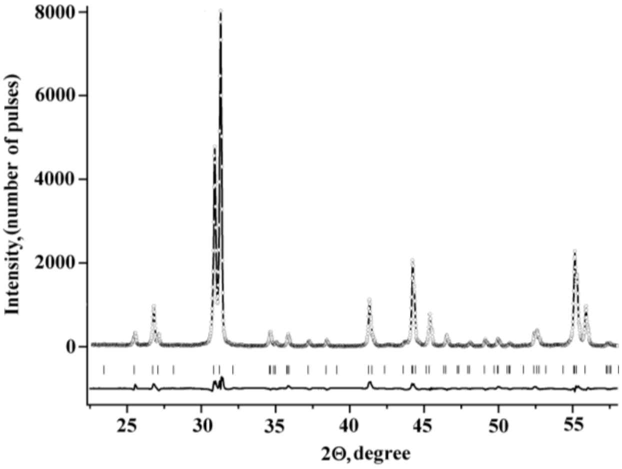

Fig. 1. Experimental (circles), calculated (solid) and difference (the lowest line) diffraction patterns of $BaGd_2Sc_{1.5}In_{0.5}O_7$ (CuK_α radiation).

Preliminary estimation of atomic coordinates for the initial $BaGd_2Sc_{1.5}In_{0.5}O_7$ structure model was carried out based on known structural data for unsubstituted $BaGd_2Sc_2O_7$ compound ($P4_2/mnm$) [18]. A comparison of experimental and calculated intensities for this structural model showed their satisfactory convergence. The results of model refinement are given in table 1, 2. The defined substance composition corresponds to the experimentally determined within the error of calculations.

$BaGd_2Sc_{1.5}In_{0.5}O_7$ SPS is formed by two-dimensional (infinite in the *XY* plane) perovskite-like blocks, which consist of two slabs of $(Sc,In)O_6$ octahedra connected by vertices (Fig. 2a) with a slab of GdO_9 polyhedra in between.

$(Sc,In)O_6$ octahedra are connected in blocks only by vertices, and each octahedron has five common vertices with adjacent octahedra of the same block. Adjacent blocks are offset relative to each other by half-edges of the perovskite cube in the direction of the diagonal of the *XY* plane and alternate along the *Z* axis.

There is no direct connection between the octahedra of adjacent blocks, they are connected by bonds
– O – Gd – O –. Of the nine oxygen atoms of the GdO_9 polyhedron, eight (4O2, 2O3, 1O4, 1O5) belong to one perovskite-like block, and the ninth oxygen atom (O2) belongs to an adjacent block (Fig. 2b). The length of this Gd – O2 interblock bond (0.207(1) nm) is significantly shorter than the known Ba – O distances, which indicates the ordered localization of large Ba atoms only in the 4f position in the cuboctahedral voids inside the perovskite-like block and correlates with the data of authors [18] on the distribution of Ba and Gd atoms in $BaGd_2Sc_2O_7$ SPS.

Determination of the nature of the distribution of Ba and Gd atoms on the 4*f* and 8*j* crystallographic positions in $BaGd_2Sc_{1.5}In_{0.5}O_7$ SPS was also carried out by calculating the values of the bond valence sums (BVS) of

Table 1.

Crystallographic data of $BaGd_2Sc_{2-x}In_xO_7$ (x = 0 and 0.5)

Position	Atom	$BaGd_2Sc_2O_7$ [18]				$BaGd_2Sc_{1.5}In_{0.5}O_7$			
		*	*X*	*Y*	*Z*	*	*X*	*Y*	*Z*
4*f*	Ba	1	0.2673(4)	0.2673(4)	0	1	0.2564(3)	0.25643(3)	0
8*j*	Gd	1	0.2713(3)	0.2713(3)	0.1865(2)	1	0.2761(3)	0.2761(3)	0.1856(2)
8*j*	Sc	1	0.2624(3)	0.2624(3)	0.3917(2)	0.75	0.2625(3)	0.2625(3)	0.3960(3)
8*j*	In	-	-	-	-	0.25	0.2625(2)	0.2625(2)	0.3960(3)
4*g*	O1	1	0.780(2)	0.220(2)	0	1	0.780(2)	0.220(2)	0
8*j*	O2	1	0.198(3)	0.198(3)	0.286(2)	1	0.198(2)	0.198(2)	0.284(3)
8*h*	O3	1	0	0.5	0.110(2)	1	0	0.5	0.114(2)
4*e*	O4	1	0	0	0.150(3)	1	0	0	0.146(2)
4*e*	O5	1	0	0	0.401(3)	1	0	0	0.400(3)
Space group		*P*4$_2$/*mnm* (№ 136)				*P*4$_2$/*mnm* (№ 136)			
Parameters of crystal lattice (nm)		*a* = 0.5776(1) *c* = 1.9941(6)				*a* = 0.57970(5) *c* = 1.9998(2)			
Independent reflections		127				85			
Total isotropic factor *B* (nm^2)		$0.39(3) \cdot 10^{-2}$				$1.50(4) \cdot 10^{-2}$			
Reliability factor, R_w		$R_W = 0.053$				$R_W = 0.052$			

Note: * - position filling.

Table 2.

Interatomic distances (d), deformation degree (Δ) of polyhedra BaO_{12}, GdO_9, and $(Sc,In)O_6$ in SPS $BaGd_2Sc_2O_7$ and $BaGd_2Sc_{1.5}In_{0.5}O_7$

Atoms	$BaGd_2Sc_2O_7$ [18]	$BaGd_2Sc_{1.5}In_{0.5}O_7$	Atoms	$BaGd_2Sc_2O_7$ [18]	$BaGd_2Sc_{1.5}In_{0.5}O_7$
	d, nm	d, nm		d, nm	d, nm
Ba – 2O1	0.283(1)	0.277(2)	Gd – 1O5	0.256(1)	0.251(2)
Ba – 2O5	0.274(1)	0.283(1)	Gd – 2O2	0.336(2	0.341(3)
Ba – 2O1	0.297(2)	0.304(2)	Gd – O_{aver}	0.265	0.265
Ba – 4O3	0.300(2)	0.307(2)	Δ GdO_9	$237 \cdot 10^{-4}$	$259 \cdot 10^{-4}$
Ba – 2O4	0.370(3)	0.360(3)	B^{III} – 2O3	0.205(1)	0.206(1)
Ba – O_{aver}	0.304	0.306	B^{III} – 1O1	0.216(2)	0.209(2)
Δ BaO_{12}	$103 \cdot 10^{-4}$	$76 \cdot 10^{-4}$	B^{III} – 1O4	0.211(2)	0.212(1)
Gd – 1O2*	0.207(1)	0.207(1)	B^{III} – 1O5	0.215(2)	0.215(2)
Gd – 1O4	0.233(2)	0.240(2)	B^{III} – 1O2	0.217(3)	0.230(3)
Gd – 2O2	0.253(2)	0.253(1)	B^{III} – O_{aver}	0.211	0.213
Gd – 2O3	0.256(3)	0.251(2)	$\Delta B^{III}O_6$	$7 \cdot 10^{-4}$	$15 \cdot 10^{-4}$

Notes: *- is the interblock distance; for $BaGd_2Sc_2O_7$ B^{III} = Sc, for $BaGd_2Sc_{1.5}In_{0.5}O_7$ B^{III} = (Sc, In); 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) [22].

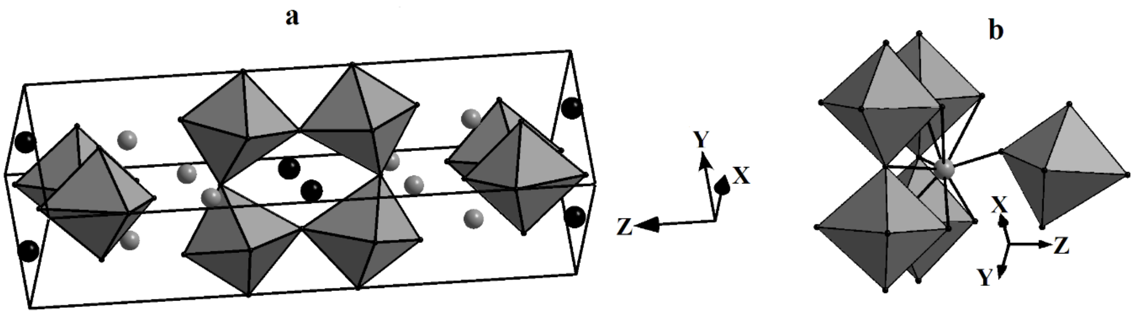

Fig. 2. Crystal structure of $BaGd_2Sc_{1.5}In_{0.5}O_7$ in the form of $(Sc,In)O_6$ octahedra, Gd atoms (gray circles) and Ba atoms (dark circles) (a) and the structure of the interblock boundary in $BaGd_2Sc_{1.5}In_{0.5}O_7$ with SPS in the form of $(Sc,In)O_6$ octahedra and Gd atoms (gray circle) (b).

these atoms in the probable BaO_{12}, BaO_9 and GdO_{12}, GdO_9 polyhedra. The bond valence (s) was calculated by the formula $s = \exp((R_0 - R)/B)$ [23], where R_0 is the tabulated value of a monovalent bond length (nm), *R* is the experimental value of a bond length (nm), and *B* (0.037 nm) is the tabulated value of a dispersion of bond lengths, which was applied for R_0 estimation.

BVS was calculated by summing up the valences of all *Me* - O bonds: BVS = $\Sigma s \cdot n$, where n is the number of bonds of this type. Analysis of the values obtained for BVS of Ba and Gd atoms in MeO_{12} (position 4*f*) and MeO_9 (position 8*j*) polyhedra (Table 3) showed that, unlike the location of Ba atoms in the 4*f* position and Gd atoms in the 8*j* position, BVS of Ba and Gd atoms in the hypothetical BaO_9 and GdO_{12} polyhedra differ significantly from their chemical valences.

Table 3.

The calculated values of bond valence sums for Ba and Gd atoms in MeO_n polyhedra of SPS $BaGd_2Sc_2O_7$ and $BaGd_2Sc_{1.5}In_{0.5}O_7$.

Composition	BVS			
	Position 4*f*		Position 8*j*	
	Polyhedron		Polyhedron	
	BaO_{12}	GdO_{12}	BaO_9	GdO_9
$BaGd_2Sc_2O_7$ [18]	1.98	1.09	5.24	2.89
$BaGd_2Sc_{1.5}In_{0.5}O_7$	1.79	0.99	5.28	2.91

Note. The value of R_0 for the Ba – O bond is 0.2285 nm, for the Gd – O bond R_0 = 0.2065 nm [23].

Results of the calculations confirm the conclusion made from analysis of *Me* – O bond lengths on the completely ordered placement of Ba and Gd atoms in $BaGd_2Sc_{1.5}In_{0.5}O_7$ SPS with the localization of Ba atoms only in intrablock voids of the perovskite-like block, and Gd atoms placement only in the GdO_9 polyhedra at the edges of blocks.

Analysis of the data obtained in this work on the structure of $BaGd_2Sc_{1.5}In_{0.5}O_7$ and structure of $BaGd_2Sc_2O_7$ [18] showed that the inclusion of In atoms in $BaGd_2Sc_2O_7$ SPS leads to a number of changes in its structure. Thus, in $BaGd_2Sc_{1.5}In_{0.5}O_7$ SPS there is an increase (~ by two times) in the degree of deformation of $(Sc,In)O_6$ octahedra, GdO_9 interblock polyhedra, the average (Sc,In) – O bond length and a decrease in the deformation degree of BaO_{12} cuboctahedra (table 2). The nature of such changes is apparently caused by bigger size of In^{3+} cation (0.094 nm) compared to Sc^{3+} cation (0.0885 nm) [22].

Therefore, an increase in the deformation of intrablock octahedra $(Sc,In)O_6$ leads results in an increase in the deformation of GdO_9 interblock polyhedra connected to them (Table 2). It should be noted that ΔGdO_9 value is the maximum among $BaLn_2Sc_2O_7$ scandates even for unsubstituted $BaGd_2Sc_2O_7$ and is one of the largest among compounds of the $A_{n+1}B_nO_{3n+1}$ family.

An increase in the deformation degree of GdO_9 interblock polyhedra with In atoms inclusion into $BaGd_2Sc_2O_7$ SPS leads to an increase in the tension in the interblock space of the SPS, destabilizes it and makes it possible to conclude that it is this factor that determines the limitation of the region of $BaGd_2Sc_{2-x}In_xO_7$ solid solutions with SPS and the absence of $BaGd_2In_2O_7$ compound with SPS.

Apparently, a rather significant decrease in deformation degree of BaO_{12} polyhedra (Table 2) is caused by an increase in the size of the intrablock cuboctahedral voids in a two-slab perovskite-like block with an increase in the size of $(Sc,In)O_6$ octahedra connected by vertices.

The inclusion of big In atoms in $BaGd_2Sc_2O_7$ SPS did not lead to a change in the length of the Gd – O interblock distance (Table 2), although in the $SrLa_2Sc_{2-x}In_xO_7$ SPS it decreases with an increase in the substitution degree of of Sc atoms [16]. The probable reason for this is the fact that the length of the Gd – O interblock distance for $BaGd_2Sc_2O_7$ is already the smallest among all known $BaLn_2Sc_2O_7$ scandates (Ln = La – Gd) with SPS [18]. Further decrease in the length of the interblock distance is impossible, as it results in the destruction of $BaLn_2Sc_2O_7$ (Ln = Tb, Dy) SPS due to connection of adjacent two-slab perovskite-like blocks with the formation of a three-dimensional perovskite structure [18].

Conclusions

Thus, in this paper, the structure of the isovalently substituted barium-gadolinium scandatoindate $BaGd_2Sc_{2-x}In_xO_7$ with x = 0.5 is determined. Analysis of the structural data obtained has shown that this type of substitution leads to an increase in the deformability of the main elements of the SPS, which can be used for further controlled regulation of the functional (electrophysical, optical, and other) structurally dependent properties of $BaGd_2Sc_{2-x}In_xO_7$ phases.

Aknowledgements

The authors thank the Ministry of Education and Science of Ukraine for financial support (project 0122U001959). Dr. O. Nakonechna is grateful to Swiss National Science Foundation (SNSF) for financial support.

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Effect of scandium atoms substitution on the two-slab structure of scandate $BaGd_2Sc_2O_7$

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Вплив заміщення атомів скандію на будову двошарової структури скандату $BaGd_2Sc_2O_7$

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Методом рентгенівської порошкової дифракції визначена тетрагональна (просторова група $P4_2/mnm$ (№ 136)) кристалічна структура ізовалентнозаміщеної фази $BaGd_2Sc_{2-x}In_xO_7$ з $x = 0{,}5$. Кристалічна структура $BaGd_2Sc_{1,5}In_{0,5}O_7$ складається з двовимірних перовськітоподібних блоків товщиною в два шари зв'язаних вершинами октаедрів $(Sc,In)O_6$. Між блоками розташований шар поліедрів GdO_9. Безпосередні зв'язки (Sc,In) – O – (Sc,In) між октаедрами суміжних блоків відсутні. Вони „зшиті" між собою за допомогою – O – Gd – O – зв'язків. Атоми Ba впорядковано розміщені лише в кубооктаедричних пустотах перовськітоподібного блоку, а їх координаційне число дорівнює 12. Аналіз кристалохімічних характеристик $BaGd_2Sc_2O_7$ та $BaGd_2Sc_{1,5}In_{0,5}O_7$ показав, що при ізовалентному заміщенні атомів Sc на більші атоми In в шаруватій перовськітоподібній структурі відбувається збільшення ступенів деформації октаедрів $(Sc,In)O_6$, міжблокових поліедрів GdO_9, середньої довжини зв'язку (Sc,In) – O та зменшення ступеня деформації кубооктаедрів BaO_{12}. Такі зміни призводять до дестабілізації шаруватої перовськітоподібної структури і обумовлюють обмеженість області твердих розчинів $BaGd_2Sc_{2-x}In_xO_7$ та відсутність сполуки $BaGd_2In_2O_7$.

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