Crystal Structure of Solid Solutions in the Sm_2O_3 -CaO-MO and Ln_2O_3 -SrO-MO Systems (Ln = Sm, Gd; M = Fe, Co)¹

L. V. Khvostova^{*a*}, A. P. Galayda^{*a*}, A. V. Maklakova^{*a*}, A. S. Baten'kova^{*a*}, A. A. Startseva^{*a*}, N. E. Volkova^{*a*}, *, L. Ya. Gavrilova^{*a*}, and V. A. Cherepanov^{*a*}

^aInstitute of Natural Science and Mathematics, Ural Federal University, Yekaterinburg, 620000 Russia *e-mail: nadezhda.volkova@urfu.ru

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Abstract—Complex oxides in the Sm₂O₃—CaO—MO and Ln₂O₃—SrO—MO systems (Ln = Sm, Gd; M = Fe, Co) were prepared via the glycerol-nitrate technique at 1100°C in air. The homogeneity ranges for the solid solutions were determined as follows: Sr_{1-x}Gd_xCoO_{3- $\delta}$ (0.1 $\leq x \leq 0.4$); Sr_{2-y}Gd_yCoO_{4- δ} (0.8 $\leq y \leq 1.2$); Sr_{1-x}Gd_xFeO_{3- δ} (0.05 $\leq x \leq 0.30$ and 0.80 $\leq x \leq 1.0$); Ca_{1-x}Sm_xFeO_{3- δ} (0.70 $\leq x \leq 1.0$); Sr_{2-y}Sm_yFeO_{4- δ} (0.7 $\leq y \leq 0.8$); Sr_{2-y}Gd_yCoO_{4- δ} (0.5 $\leq z \leq 0.30$ and 0.80 $\leq x \leq 1.0$); Ca_{2-y}Sm_yFeO_{4- δ} (y = 0.90); Sr_{3-z}Sm_zFe₂O_{7- δ} (0 $\leq z \leq 0.3$ and z = 1.8); and Sr_{3-z}Gd_zFe₂O_{7- δ} (0 $\leq z \leq 0.3$ and z = 1.9). For all single phase oxides, the crystal structure was determined and the unit cell parameters, the unit cell volume, and the structural parameters were refined.}

Keywords: complex oxides, perovskites, Ruddlesden-Popper phases, X-ray diffraction analysis, crystal structure **DOI:** 10.1134/S0020168519080041

INTRODUCTION

Complex oxide materials with mixed electronic and ionic conductivity are widely used as fuel cell electrodes [1-5], oxygen membranes [6-8], exhaust gases catalysts [9, 10], etc. The Ruddlesden-Popper phases with the general formula $A_{n+1}B_nO_{3n+1}$, where the A position is occupied by a lanthanide and/or an alkaline earth element and the B position is occupied by 3dmetals (Mn, Fe, Co), are objects of particular interest. Their structure is constructed by alternation of the perovskite layers (ABO_3) with the rock salt layers [11]. In this respect ABO₃ perovskites can be treated as the limiting homolog of the series with $n = \infty$. The physicochemical properties of these oxides substantially depend on the crystal structure; therefore, its detailed description, as well as information about the preparation route and the homogeneity ranges, is necessary for the successful utilization of such materials.

The present work aims to determine the influence of the nature of atoms of the A and B sites and their concentration on the homogeneity ranges and the crystal structure of the phases formed in the Sm_2O_3 -CaO-MO and Ln_2O_3 -SrO-MO systems (Ln = Sm, Gd; M = Fe, Co).

EXPERIMENTAL

The samples were prepared by the glycerol-nitrate technique. The starting reagents for the preparation of samples were samarium oxide Sm₂O₃ (SmO-L), gadolinium oxide Gd₂O₃ (GdO-L), calcium carbonate $CaCO_3$ (analytical grade), strontium carbonate $SrCO_3$ (analytical grade), iron oxalate $FeC_2O_4 \cdot 2H_2O$ (analytical grade), and also metallic cobalt, nitric acid (special purity grade), and glycerol (analytical grade). Metallic cobalt was obtained by reduction of Co₃O₄ (special purity grade) at 600°C in a flow of hydrogen. The weights of the initial components were dissolved in 4 M HNO₃ under heating; then glycerol was added; the obtained solution was evaporated in a porcelain dish. After dehydration, the viscous gel was transformed into brown powder. The dry residue was heated stepwise to a temperature of 1100°C. The total annealing time at 1100°C in air was 120 h. After the final annealing, the samples were slowly cooled down to room temperature (cooling rate $100^{\circ}C/h$).

The phase composition was determined using a Shimadzu XRD-7000 diffractometer (Cu K_{α} radiation, angle range $2\theta = 20^{\circ}-90^{\circ}$, step $0.01^{\circ}-0.04^{\circ}$, exposure time 2-10 s) at room temperature in air. Phase identification was performed using the ICDD database. The structure was refined by the full-profile Rietveld method using Fullprof 2008 software.

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Fig. 1. The XRD pattern for $Sr_{1,2}Gd_{0,8}CoO_{4+\delta}$ refined by the full-profile Rietveld method. Points are the experimental data; solid upper line is the calculated profile; solid lower line is the difference between the experimental data and the calculated profile.

RESULTS AND DISCUSSION

Sm_2O_3 -CaO-CoO and Ln_2O_3 -SrO-CoO Systems (Ln = Sm, Gd)

According to the results of X-ray diffraction (XRD), it is found that only a solid solution series with the K₂NiF₄-type structure is formed in the Sm₂O₃-CaO-CoO system [12]. When calcium is replaced by the larger size strontium, a second series of solid solutions Sr_{1-x}Ln_xCoO_{3- $\delta}$ with the perovskite structure is formed in addition to Sr_{2-v}Ln_vCoO_{4- δ}.}

The crystal structure of $M_{2-y}Ln_yCoO_{4-\delta}$ (M = Ca, Sr). The homogeneity range of the $Ca_{2-y}Sm_yCoO_{4-\delta}$ solid solution at 1100°C in air corresponds to the interval of $1.0 \le y \le 1.2$ [12], while in the Sr-containing systems annealing under these conditions leads to the formation of $Sr_{2-y}Ln_yCoO_{4-\delta}$ solid solutions (Ln = Sm³⁺, Gd³⁺) with wider homogeneity ranges: $0.9 \le y \le 1.3$ [13] and $0.8 \le y \le 1.2$ for Ln = Sm and Gd, respectively.

The crystal structure of complex oxides $Ca_{2-y}Sm_{y}$ -CoO_{4- δ} significantly depends on the concentration of samarium ions. The XRD pattern for CaSmCoO_{4- δ} was refined within the tetragonal cell (sp. gr. *I*4/*mmm*). An increase in Sm³⁺ content in Ca_{2-y}Sm_yCoO_{4- δ} (*y* = 1.1–1.2) leads to a change in the crystal structure to orthorhombic (sp. gr. *Bmab*) [12].

All single phase $Sr_{2-y}Ln_yCoO_{4-\delta}$ solid solutions crystallized in the tetragonal cell, sp. gr. *I*4/*mmm*. As an example, Fig. 1 shows the XRD pattern for

 $Sr_{1.2}Gd_{0.8}CoO_{4+\delta}$, refined by the full-profile Rietveld method.

On the basis of the XRD data, the structural parameters were calculated for all single-phase samples. An increase in samarium or gadolinium ion concentration in $\text{Sr}_{2-y}\text{Ln}_y\text{CoO}_{4+\delta}$ leads to a gradual decrease in the *c* parameter of the unit cell, while the *a* parameter varies insignificantly. This trend can be explained in terms of the size effect ($r_{\text{Sm}^{3+}} = 1.24 \text{ Å}$, $r_{\text{Sc}^{2+}} = 1.44 \text{ Å}$, $r_{\text{Gd}^{3+}} = 1.11 \text{ Å} [14]$) (Fig. 2).

The crystal structure of $Sr_{1-x}Ln_xCoO_{3-\delta}$. Earlier James et al. [15] showed that the crystal structure of $Sr_{1-x}Ln_xCoO_{3-\delta}$ significantly depends on the lanthanide content and lanthanide radius. Introduction of rare earth ions with medium radii (such as samarium and gadolinium) results in the ordering of Ln^{3+} and Sr^{2+} cations in the A sublattice and oxygen vacancies that leads to the formation of the $2a_p \times 2a_p \times 4a_p$ superstructure (where a_p is the unit cell parameter of the cubic perovskite). The unit supercell contains three nonequivalent A positions, which are filled successively with a gradual increase in the samarium concentration. At x < 0.25, Sm³⁺ ions fill the A1 sites, while the A2 and A3 positions remain fully occupied by Sr^{2+} ions. Further increase in the samarium content leads to substitution in the A3 positions, while A1 and A2 are fully occupied by Sm³⁺ and Sr²⁺ ions respectively.

According to the XRD data, it is found that the single-phase complex oxides $Sr_{1-x}Sm_xCoO_3 - \delta$ form



Fig. 2. The unit cell parameters versus composition of the $Sr_{2-\nu}Gd_{\nu}CoO_{4-\delta}$ solid solution (0.8 $\leq y \leq$ 1.2).

within the composition range $0.05 \le x \le 0.50$ [13]. When replacing Sm³⁺ with Gd³⁺, the homogeneity range becomes narrower ($0.1 \le x \le 0.4$), which can be explained by an increase in the difference between the radii of strontium and lanthanide ions ($r_{\text{Sm}^{3+}} = 1.24 \text{ Å}$; $r_{\text{Gd}^{3+}} = 1.11 \text{ Å}$; $r_{\text{Sr}^{2+}} = 1.58 \text{ Å}$ [14]).

The XRD patterns for the single phase samples were refined within the framework of the tetragonal cell $2a_p \times 2a_p \times 4a_p$, sp. gr. *I*4/*mmm*, which is consistent with the earlier reported data [13, 15, 16].

Figure 3 illustrates the dependence of the unit cell parameters for the Sr_{1-x}Gd_xCoO_{3-δ} solid solution calculated from the XRD data versus gadolinium content. The observed decrease in the unit cell parameters and unit cell volume of the complex oxides Sr_{1-x}Ln_xCoO_{3-δ} with an increase in the concentration of lanthanide ions is associated with a smaller radius of samarium and gadolinium ions compared to strontium ion ($r_{\text{Sm}^{3+}} = 1.24 \text{ Å}$, $r_{\text{Gd}^{3+}} = 1.11 \text{ Å}$, $r_{\text{Sr}^{2+}} = 1.58 \text{ Å}$ [14]).

$$Sm_2O_3$$
-CaO-FeO and Ln_2O_3 -SrO-FeO Systems
($Ln = Sm, Gd$)

Formation of three types of perovskite-like solid solutions $A_{n+1}B_nO_{3n+1}$ ($n = 1, 2, \infty$) with different range of substitution in the A sublattice was detected in the iron-containing systems.

The crystal structure of $M_{1-x}Ln_xFeO_{3-\delta}$ (M = Ca, Sr). According to the XRD data, it is established that single phase complex oxides with the perovskite structure are formed within two intervals of compositions. The solid solutions enriched in strontium $Sr_{1-x}Sm_xFeO_{3-\delta}$ (0.05 $\leq x \leq 0.30$) $x \leq 0.50$) [17] and $Sr_{1-x}Gd_xFeO_{3-\delta}$ (0.05 $\leq x \leq 0.30$) are described within the cubic unit cell, sp. gr. *Pm3m*.



Fig. 3. The unit cell parameters versus composition of the $Sr_{1-x}Gd_xCoO_{3-\delta}$ solid solution (0.1 $\leq x \leq$ 0.4).

Figure 4 shows the XRD pattern for $Sr_{0.7}Gd_{0.3}FeO_{3-\delta}$ refined by the Rietveld method as an example.

Slightly larger unit cells of the rare earth ferrites LnFeO₃ in comparison with cobaltites LnCoO₃ [12] allow partial replacement of Ln³⁺ with larger alkaline earth ions Ca²⁺ and Sr²⁺. The solid solutions with a high lanthanide content Ca_{1-x}Sm_xFeO_{3-\delta} (0.70 $\le x \le 1.0$), Sr_{1-x}Sm_xFeO_{3-\delta} (0.85 $\le x \le 1.0$), and Sr_{1-x}Gd_xFeO_{3-\delta} (0.80 $\le x \le 1.0$) crystallize in the orthorhombic cell (sp. gr. *Pbnm*), which is isostructural to the samarium and gadolinium ferrites LnFeO_{3-\delta}.

The unit cell parameters and the unit cell volumes, as well as the atomic coordinates, were calculated for all single phase samples. The results for the $Ca_{1-x}Sm_xFeO_{3-\delta}$ solid solutions are listed in Table 1 as an example.



Fig. 4. The XRD pattern for $Sr_{0.7}Gd_{0.3}FeO_{3-\delta}$ refined by the full-profile Rietveld method.

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Table 1. The unit cell parameters and atom coordinates for the solid solutions of $Ca_{1-x}Sm_xFeO_{3-\delta}$ (sp. gr. *Pbnm*): Ca/Sm-(x, y, 0.25); Fe-(0.5, 0, 0); O1-(x, y, 0.25); O2-(x, y, z) and $Ca_{1.1}Sm_{0.9}FeO_{4-\delta}$ (sp. gr. *Bmab*): Ca/Sm-(0, y, z); Fe-(0, 0, 0); O1-(0.25, 0.25, z); O2-(0, y, z)

Sample			Ca. Sm. FeO.			
		x = 1.0	x = 0.9	x = 0.8	x = 0.7	Cu _{1.1} 0110.91 CO ₄ = 8
<i>a</i> , Å		5.401(1)	5.399(1)	5.398(1)	5.399(1)	5.386(1)
<i>b</i> , Å		5.591(1)	5.567(1)	5.552(1)	5.544(1)	5.448(1)
<i>c</i> , Å		7.710(1)	7.696(1)	7.689(1)	7.686(1)	12.030(2)
$V, Å^3$		232.80(2)	231.34(2)	230.45(2)	230.08(2)	353.00(2)
R _{Br} , %		5.51	5.09	5.53	4.79	6.31
<i>R</i> _{<i>f</i>} , %		8.98	9.36	8.44	9.53	6.22
x	Sm	0.0131	0.0099	0.0089	0.0085	0.0000
у		-0.0557	-0.0526	-0.0510	-0.0503	-0.0123
z		0.2500	0.2500	0.2500	0.2500	0.3565
x	O1	-0.0837	-0.0853	-0.0832	-0.0637	0.2500
у		0.5260	0.5264	0.5209	0.5130	0.2500
z		0.2500	0.2500	0.2500	0.2500	-0.0190
x	O2	-0.2008	-0.2121	-0.2082	-0.2043	0.0000
у		0.2237	0.2271	0.2184	0.2054	0.0474
z		0.0458	0.0460	0.0424	0.0530	0.7350

The concentration dependences for the unit cell parameters and the unit cell volume of the $Ca_{1-x}Sm_{x}$ -FeO_{3- δ} solid solutions are shown in Fig. 5. The decrease in the unit cell parameters is associated with an increase in the mean oxidation state of iron with the rise of calcium content in the samples ($r_{Fe^{3+}} = 0.645$ Å, $r_{Fe^{4+}} = 0.585$ Å [14]). Similar dependences were obtained for the complex oxides $Sr_{1-x}Ln_xFeO_{3-\delta}$.

The crystal structure of $M_{2-y}Ln_yFeO_{4-\delta}$ (M = Ca, Sr). According to the XRD data, single-phase complex oxides $Sr_{2-y}Sm_yFeO_{4-\delta}$ are formed at y = 0.7-0.8, and $Sr_{2-y}Gd_yFeO_{4-\delta}$ at y = 0.75-0.80; both Sm- and Gd-containing solid solutions have the tetragonal structure (sp. gr. *I4/mmm*). The only oxide in the Ca_{2-y}- $\text{Sm}_{y}\text{FeO}_{4-\delta}$ series which exhibits the orthorhombic structure (sp. gr. *Bmab*) (Fig. 6) is formed at y = 0.90. It should be noted that ferrites with the K₂NiF₄-type structure have a narrower homogeneity range compared to that for cobaltites.

Figure 6 illustrates the model of crystal structure constructed using the Diamond 3.2 software package together with the XRD pattern for $Ca_{1.1}Sm_{0.9}FeO_{4-\delta}$, refined by the full-profile Rietveld method.

The unit cell parameters for $Sr_{2-y}Ln_yFeO_{4-\delta}$ calculated from the XRD data are listed in Table 2.

The crystallographic parameters for $Ca_{1,1}Sm_{0,9}FeO_{4-\delta}$ refined by the Rietveld method from the XRD data are listed in Table 1.



Fig. 5. The unit cell parameters (a) and unit cell volume (b) for $Ca_{1-x}Sm_{x}FeO_{3-\delta}$ versus concentration.

The crystal structure of $Sr_{3-z}Ln_zFe_2O_{7-\delta}$. In order to establish the possibility of formation of substituted ferrites $Sr_{3-z}Ln_zFe_2O_{7-\delta}$, the samples with z = 0.3-2.2 were synthesized.



Fig. 6. The XRD pattern for $Ca_{2-y}Sm_yFeO_{4-\delta}$ (y = 1.1) refined by the Rietveld method; the inset shows the model of the unit cell of oxide constructed with the help of the Diamond 3.2 software package.

According to the XRD data, complex oxides $Sr_{3-z}Sm_zFe_2O_{7-\delta}$ are formed in the range of compositions $0 \le z \le 0.3$ and at z = 1.8, and $Sr_{3-z}Gd_zFe_2O_{7-\delta}$ at $0 \le z \le 0.3$ and z = 1.9. The XRD patterns for the $Sr_{3-z}Ln_zFe_2O_{7-\delta}$ solid solutions (z = 0-0.3) much like the unsubstituted ferrite $Sr_3Fe_2O_{7-\delta}$ are satisfactorily described within the tetragonal cell (sp. gr. *I4/mmn*). The structure of $Sr_{1.2}Sm_{1.8}Fe_2O_{7-\delta}$ [18] and $Sr_{1.1}Gd_{1.9}Fe_2O_{7-\delta}$ was described in the framework of the tetragonal symmetry (sp. gr. *P*4₂/*mnm*), which is consistent with the data obtained for Nd₂SrFe₂O_{7-\delta} [19].

Figure 7 demonstrates the XRD pattern for $Sr_{1.1}Gd_{1.9}Fe_2O_{7-\delta}$ refined by the full-profile Rietveld method.

The unit cell parameters of single-phase Sr_{3-z} - $Ln_zFe_2O_{7-\delta}$ calculated from the XRD data are listed in Table 2.

	-		z = y = y			
Composition	sp. gr.	a, Å	c, Å	<i>V</i> , Å ³	R _{Br} , %	$R_{f}, \%$
$\overline{Sr_{1.3}Sm_{0.7}FeO_{4-\delta}}$	I4/mmm	3.825(1)	12.577(1)	184.05(2)	7.83	5.66
$Sr_{1.2}Sm_{0.8}FeO_{4-\delta}$	I4/mmm	3.816(1)	12.596(1)	183.38(2)	7.24	5.07
$Sr_{2.7}Sm_{0.3}Fe_{2}O_{7-\delta}$	I4/mmm	3.869(1)	20.08(1)	300.57(2)	0.952	1.23
$Sr_{1.2}Sm_{1.8}Fe_2O_{7-\delta}$	P4 ₂ /mnm	5.489(1)	20.014(1)	602.81(2)	7.54	7.85
$Sr_{1.25}Gd_{0.75}FeO_{4-\delta}$	I4/mmm	3.817(1)	12.547(1)	182.83(2)	4.25	3.68
$Sr_{1.2}Gd_{0.8}FeO_{4-\delta}$	I4/mmm	3.822(1)	12.524(1)	182.99(2)	4.35	3.84
$Sr_{2.7}Gd_{0.3}Fe_2O_{7-\delta}$	I4/mmm	3.870(1)	20.076(1)	300.74(2)	1.94	2.63
$Sr_{1.1}Gd_{1.9}Fe_2O_{7-\delta}$	P4 ₂ /mnm	5.493(1)	19.821(1)	598.06(2)	0.64	0.72

Table 2. The unit cell parameters and unit cell volume for $Sr_{2-y}Ln_yFeO_{4-\delta}$ and $Sr_{3-z}Ln_zFe_2O_{7-\delta}$



Fig. 7. The XRD pattern for $Sr_{1.1}Gd_{1.9}Fe_2O_{7-\delta}$ refined by the Rietveld method.

CONCLUSIONS

The formation of perovskite-like solid solutions $A_{n+1}B_nO_{3n+1}$ of three types $(n = 1, 2, \infty)$ in the Sm_2O_3 -CaO-MO and Ln_2O_3 -SrO-MO systems (Ln = Sm, Gd; M = Fe, Co) with varying of degrees of substitution in the A sublattice was established by XRD. A crystal structure for all single-phase oxides was determined and the unit cell parameters and the atomic coordinates were refined. It is shown that the unit cell parameters and the unit cell parameters with the rise in concentration of lanthanide ions.

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