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Structure peculiarities of the $La_{1-x}Nd_xGaO_3$ solid solutions

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Abstract

The $LaGaO_3$–NdGaO3 pseudobinary system was investigated in the concentration range 0–53 at.% Nd by means of X-ray structural and phase analysis. The $La_{1-x}Nd_xGaO_3$ solid solutions exist in the whole investigated concentration region. The lattice constants change with increasing Nd content: a decreases from 5.52266(6) to 5.46754(7) Å, and c from 7.7713(1) to 7.74241(9) Å, whereas b increases from 5.49047(7) to 5.49118(6) Å. There are four ranges of $La_{1-x}Nd_xGaO_3$ solid solutions characterized by different relations between the Perovskite-like cell parameters: **I** ($0<x<0.225$) with $a_p>c_p>b_p$; **II** ($0.225<x<0.32$) with $a_p>b_p>c_p$; **III** ($0.32<x<0.39$) with $b_p>a_p>c_p$; and **IV** ($0.39<x<1$) with $b_p>c_p>a_p$.

Keywords: Insulators; Ferroelectrics; Crystal growth; Crystal structure and symmetry; X-ray diffraction

1. Introduction

Lanthanum and neodymium gallates are promising substrate materials for epitaxy of high-temperature superconductors (HTSC) and Perovskites exhibiting colossal magnetoresistance (CMR) [1,2]. Both gallates adopt an orthorhombically distorted Perovskite-like structure with the following lattice parameters at room temperature: $a=5.4276(1)$ Å, $b=5.4979(1)$ Å, $c=7.7078(2)$ Å for $NdGaO_3$; and $a=5.52266(6)$ Å, $b=5.49047(7)$ Å, $c=7.7713(1)$ Å for $LaGaO_3$ [3–5]. $LaGaO_3$ is exceptional among numerous compounds with the GdFeO3 structure, because its lattice parameters $a>b$, whereas in other compounds, including $NdGaO_3$, $a<b$. Therefore, formation of solid solutions with pseudotetragonal or pseudocubic structures should be expected in the $LaGaO_3$–$NdGaO_3$ pseudobinary system. The aim of the present work is to investigate in detail the $La_{1-x}Nd_xGaO_3$ solid solutions using X-ray structural and phase analysis.

2. Experimental

The samples for investigation — $La_{1-x}Nd_xGaO_3$ single crystals with $x=0$, 0.07, 0.12, 0.17, 0.20, 0.27, 0.32, 0.37, 0.44 and 0.53 — were grown using the Czochralski method. The growth procedure was described in detail in Ref. [6]. The structure of the crystals was investigated using the X-ray powder diffraction method. This method was used instead of the single-crystal diffraction technique because of the twinning effect that occurs in all these materials and makes it impossible to prepare twin-free single-domain samples needed for the single-crystal diffraction method. The diffraction measurements were made using the DRON-3 powder diffractometer. We used CuKα radiation applying the $\theta/2\theta$ scanning mode in the 19–140° 2θ range with a step width of 0.02° and a counting time of 10 s/step.

The experimental data were analyzed using the full profile Rietveld refinement method. All calculations were performed using the CSD (Crystal Structure Determination) program package [7]. It includes refinement of lattice parameters, positional and thermal parameters, scaling factor, zero shift, background parameter and Bragg-peak profile parameter, together with one parameter for the extinction correction.

3. Results and discussion

The X-ray analysis of $La_{1-x}Nd_xGaO_3$ solid solutions showed that all crystals adopted a Perovskite-like structure. The full-profile refinement in the space group *Pbnm* ($Z=$

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4) using atom coordinates in $LaGaO_3$ and $NdGaO_3$ lattices [5] as the starting positions gave excellent fits for experimental and calculated profiles for all samples. The thermal parameters were refined anisotropically for rare-earth cations and isotropically for all other ions. Sites occupancy was fixed according to the stoichiometry under the assumption of a substitutional solid solution of Nd and La at the 4*c* site. An excellent fit of the calculated curves to the experimental diffractograms was obtained in the case of all samples. The obtained values of lattice constant, positions of atoms, atom thermal parameters and the final *R*-factor values are given in Table 1.

The lattice constants *a* and *c* of the $La_{1-x}Nd_xGaO_3$ solid solutions decrease, whereas the *b* parameter slightly increases with increasing Nd content (see Fig. 1). There are four ranges of *x* in this system characterized by various relations between Perovskite-like cell parameters: (i) ($0<x<0.225$) with $a_p>c_p>b_p$; (ii) ($0.225<x<0.32$) with $a_p>c_p>b_p$; (iii) ($0.32<x<0.39$) with $b_p>a_p>c_p$; and (iv) ($0.39<x<1$) with $b_p>c_p>a_p$. The composition dependence of the lattice parameters deviates from a linear one assumed by the Vegard model. A positive deviation between the experimental points and Vegard's model is observed for *c* parameters, whereas for *a* and *b* constants negative deviations are visible. However, the unit cell volume decreases linearly with increasing Nd content in accordance with Vegard's law. Small deviations from Vegard's law seen in Fig. 1 can be explained to the first approximation by an uncertainty in determining the composition of the samples.

The differences between cell parameters in the crystals

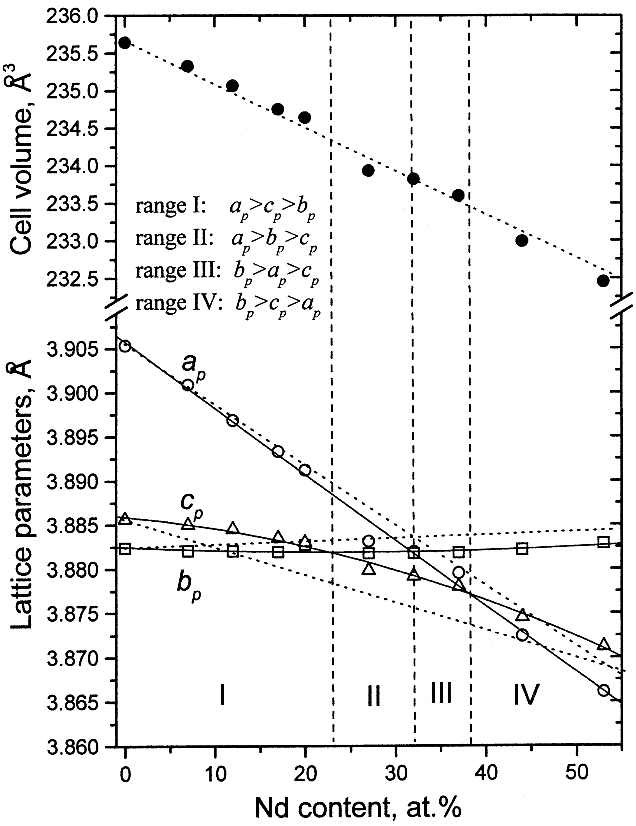

Fig. 1. The variation of the lattice parameters and unit cell volume in $La_{1-x}Nd_xGaO_3$ solid solutions as a function of Nd content. The orthorhombic lattice parameters are transformed to Perovskite-like cell parameters according to the following relations: $a_p = a_0/\sqrt{2}$, $b_p = b_0/\sqrt{2}$, $c_p = c_0/2$. The dotted lines correspond to the Vegard's model. (The cell parameters for $NdGaO_3$ are taken from [3].)

Table 1
Crystallographic data for $LaGaO_3$ and $La_{1-x}Nd_xGaO_3$ solid solutions

Atoms (sites)	Parameters	$La_{1-x}Nd_xGaO_3$ solid solutions contents, *x*									
		0	0.07	0.12	0.17	0.20	0.27	0.32	0.37	0.44	0.53
	a (Å)	5.52266(6)	5.51667(6)	5.51092(7)	5.50600(8)	5.50279(8)	5.49169(1)	5.4899(1)	5.48650(9)	5.4764(1)	5.46754(7)
	b (Å)	5.49047(7)	5.49006(7)	5.49041(7)	5.49987(8)	5.49054(8)	5.48958(9)	5.48968(8)	5.48968(8)	5.49016(8)	5.49118(6)
	c (Å)	7.7713(1)	7.77003(9)	7.76891(9)	7.7665(1)	7.7663(1)	7.7596(1)	7.7584(1)	7.7558(1)	7.7491(1)	7.74241(9)
	V ($Å^3$)	235.642(9)	235.330(8)	235.065(9)	234.74(1)	234.64(1)	233.93(1)	233.82(1)	233.60(1)	232.99(1)	232.452(8)
La(Nd)	*x*	−0.0036(3)	−0.0046(3)	−0.0042(2)	−0.0035(4)	−0.0045(3)	−0.0063(3)	−0.0056(3)	−0.0054(3)	−0.0065(3)	0.0067(3)
(*x y* 1/4)	*y*	0.0175(1)	0.0195(1)	0.0216(2)	0.0227(2)	0.0238(2)	0.0262(2)	0.0267(2)	0.0278(2)	0.0305(1)	0.0327(1)
	B(*eq*)[a]	0.88(3)	0.60(3)	0.66(3)	0.85(3)	0.59(3)	0.78(3)	0.91(4)	0.61(4)	0.80(4)	0.41(3)
Ga											
(1/2 0 0)	*B*(*eq*)[a]	0.84(7)	0.56(7)	0.62(8)	0.75(2)	0.54(2)	0.88(2)	0.90(2)	0.64(2)	0.79(3)	0.40(3)
O1	*x*	0.0665(15)	0.068(2)	0.070(3)	0.063(2)	0.074(2)	0.074(3)	0.058(2)	0.081(2)	0.071(4)	0.072(4)
(*x y* 1/4)	*y*	0.505(2)	0.499(2)	0.497(2)	0.497(2)	0.496(2)	0.498(2)	0.496(2)	0.493(2)	0.492(2)	0.498(2)
	B(*eq*)[a]	0.6(3)	0.8(2)	1.3(3)	0.7(3)	1.1(3)	1.9(4)	0.6(3)	0.8(3)	0.5(3)	0.7(4)
O2	*x*	−0.280(2)	−0.284(2)	−0.277(2)	−0.291(2)	−0.280(2)	−0.284(3)	−0.288(3)	−0.280(3)	−0.281(3)	−0.297(3)
(*x y z*)	*y*	0.281(2)	0.276(2)	0.274(2)	0.273(2)	0.280(2)	0.275(3)	0.290(2)	0.280(2)	0.286(3)	0.284(2)
	z	0.0371(9)	0.0402(11)	0.0371(12)	0.0363(14)	0.0407(11)	0.034(2)	0.0404(14)	0.0419(15)	0.030(2)	0.035(2)
	B(*eq*)[a]	0.5(2)	1.2(2)	0.5(2)	1.3(2)	0.5(2)	1.1(2)	0.9(2)	0.7(2)	0.6(2)	1.0(2)
	R_I	*0.052*	*0.048*	*0.046*	*0.053*	*0.045*	*0.051*	*0.050*	*0.050*	*0.067*	*0.047*
	R_P	*0.0794*	*0.0745*	*0.0723*	*0.0893*	*0.0778*	*0.0889*	*0.0914*	*0.0914*	*0.0933*	*0.1044*

[a] $B(eq) = 1/3[B_{11}(a^*)^2a^2 + \ldots 2B_{23}b^*c^*bc \cos \alpha]$; $T = \exp[-1/4(B_{11}(a^*)^2h^2 + \ldots 2B_{23}b^*c^*kl]$.

with $x = 0.27$ and 0.32 are so small that neither reflex splitting nor deformation were observed in the X-ray diffraction patterns. All the peaks can be indexed in the primitive cubic cell with doubled Perovskite lattice parameters $a_c = 7.7631$ Å and 7.7610 Å, respectively. However, the structure refinement in the space groups *P*23 or *Pm*3 led to a significant increase in the residual factor and to incorrect values of atom thermal parameters and some of the interatomic distances. That means that these crystals only dimensionally appear to be cubic; however, the symmetry remains orthorhombic.

The analysis of cation–anion distances in $La_{1-x}Nd_xGaO_3$ solid solutions proved that rare earth–oxygen (R–O) average distances calculated for coordination numbers (CN) 8, 9 and 10 tend to decrease with increasing x value, whereas R–O average distances for CN 12 remain constant. The La–Nd substitution also does not influence the Ga–O average distances.

The cation–cation distances are very sensitive to changes in the average R cation radii. With increasing Nd content the Ga–Ga and R–R average distances decrease, while the R–Ga distance remains almost constant (Fig. 2). It is worth noting that the minimal R–Ga distance decreases, whereas the maximal R–Ga distance essentially increases with the increase of Nd content. As we have recently shown [5], the $(R–Ga_{max})/(R–Ga_{min})$ and $(R–R_{ave})/(Ga–Ga_{ave})$ ratios can be successfully used for characterization of the Perovskite structure deformation. These ratios should be equal to 1 in cubic Perovskites. The fact that they increase with increasing x in $La_{1-x}Nd_xGaO_3$ solid solutions indicates that the Perovskite structure deformation increases accordingly. The degree of GaO_6-octahedra tilt, often used for characterization of Perovskite structure deformation, does not exhibit any regular dependence on the Nd content.

From the obtained results it can be concluded that subsitutional-type solid solutions are formed in the $LaGaO_3$–$NdGaO_3$ pseudobinary system. A positive deviation between the experimental points and Vegard's model is observed for c parameters, whereas for a and b constants negative deviations are detected. The decrease of the average R cation radius while substituting La with Nd leads to the decrease of the unit cell volume and to the increase of Perovskite structure deformation in $La_{1-x}Nd_xGaO_3$ solid solutions with increasing x.

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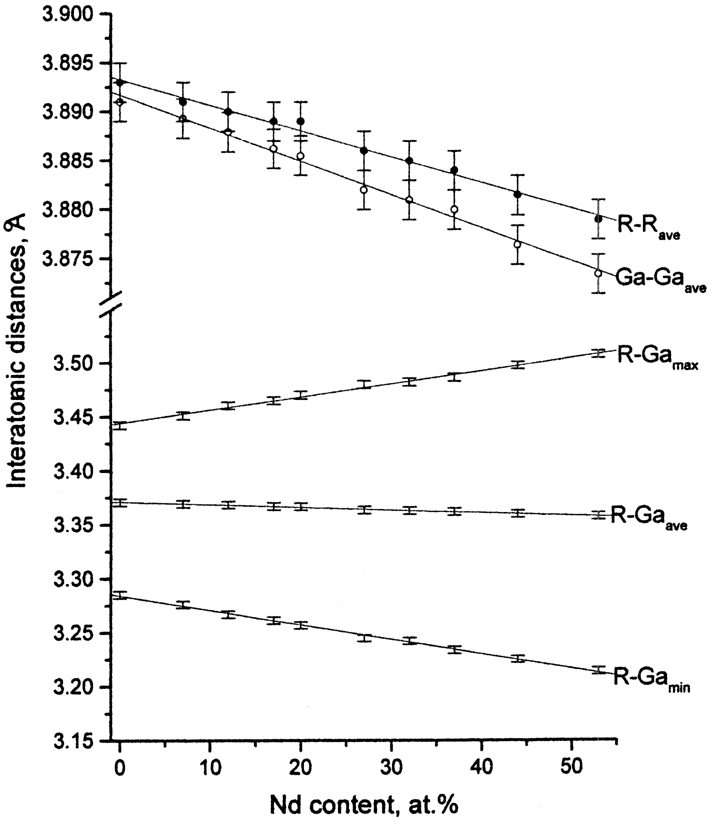

Fig. 2. The cation–cation distances in the structure of $La_{1-x}Nd_xGaO_3$ solid solutions vs. Nd content. The experimental errors in the interatomic distances are shown as vertical bars.

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