Pbnm – R-3c phase transition in $La_{0.9}Gd_{0.1}GaO_3$

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$REGaO_3$ crystals with perovskite structure are prospective substrate materials for HTSC and CMR films [1]. The one of most important aspect is absence of phase transitions in technological range of temperature. In Ref. [2] we reported the formation and crystal structure of the $La_{1-x}Gd_xGaO_3$ solid solution with orthorhombically distorted perovskite structure. In order to study the influence of La-RE substitution on the critical temperature of the phase transition, the temperature behaviour of $La_{0.9}Gd_{0.1}GaO_3$ was investigated using high resolution synchrotron X-ray diffraction in the temperature range 303 – 1173 K. The wavelength was 0.70879(5). Full patterns were collected in the 2θ - range of 7.480° - 90.036° with step size 0.004° using Image Plate detector at B2 line (HASYLAB). The values of the lattice parameters and atomic coordinates (Tab.1, 2) were refined by full-profile Rietveld method using WinCSD program package.

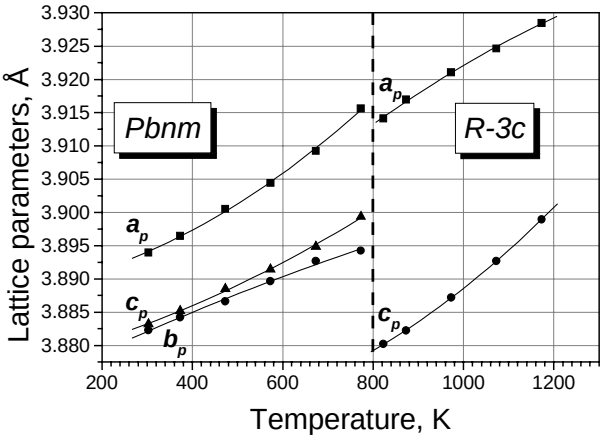
Table 1. Refined structural parameters for orthorhombic $La_{0.9}Gd_{0.1}GaO_3$ phase (sp. group *Pbnm*).

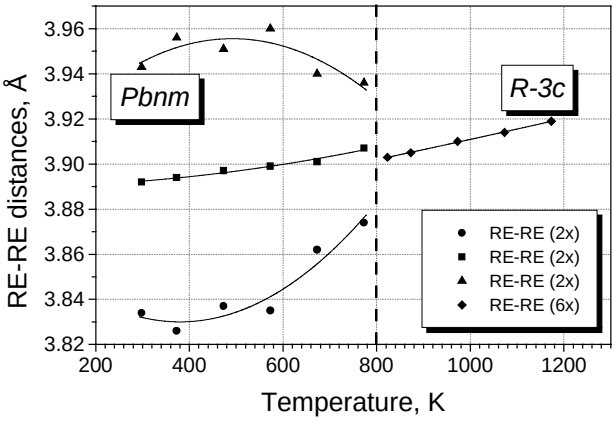
Atom, sites		RT	373 K	473 K	573 K	673 K	773 K
	a, Å	5.5069(3)	5.5104(3)	5.5162(3)	5.5217(2)	5.5285(3)	5.5375(2)
	b, Å	5.4904(3)	5.4931(3)	5.4965(2)	5.5008(2)	5.5051(2)	5.5073(3)
	c, Å	7.7664(3)	7.7703(3)	7.7770(3)	7.7829(3)	7.7897(3)	7.7987(4)
RE, 4*c*	*x*	-0.007(2)	-0.008(1)	-0.007(2)	-0.008(1)	-0.005(3)	-0.004(3)
(x y ¼)	*y*	0.0226(6)	0.0223(7)	0.0220(7)	0.0203(7)	0.0191(8)	0.0211(10)
	B(is/eq)	0.57(9)	0.72(11)	0.72(10)	0.73(10)	1.05(11)	1.05(11)
Ga, 4*b* (1/2 0 0)	*B(is/eq)*	0.60(7)	0.8(3)	0.8(2)	0.9(2)	1.1(2)	1.1(2)
O1, 4*c*	*x*	0.058(9)	0.072(9)	0.063(9)	0.069(8)	0.073(9)	0.073(9)
(0 0 ¼)	*y*	0.503(10)	0.495(12)	0.495(12)	0.496(13)	0.501(14)	0.501(14)
	B(is/eq)	0.4(9)	1.2(11)	1.6(11)	1.6(12)	1.7(12)	1.7(12)
	x	-0.284(11)	-0.282(11)	-0.279(12)	-0.277(12)	-0.270(16)	-0.270(16)
O2, 8*d*	*y*	0.273(13)	0.286(12)	0.272(13)	0.276(14)	0.270(16)	0.270(16)
(x y z)	*z*	0.041(5)	0.030(7)	0.039(5)	0.032(7)	0.034(5)	0.034(5)
	B(is/eq)	0.8(7)	1.2(7)	1.2(7)	1.4(7)	1.7(7)	1.7(7)
	R_I	0.0899	0.0833	0.0945	0.0933	0.0966	0.1415
	R_P	0.1878	0.1910	0.1915	0.2025	0.2071	0.3550

The orthorhombic-to-rhombohedral phase transition has been detected at 773 – 823 K. From the analysis of the data it is evident that La-Gd substitution led to increase of the critical temperature from 420 K in pure $LaGaO_3$ to ~800 K in $La_{0.9}Gd_{0.1}GaO_3$. This value is in good agreement with the linear dependence of the phase transition temperature in $La_{1-x}RE_xGaO_3$ (RE=Pr, Nd, Sm) perovskites on the average RE^{3+} cation radii [3]. Thermal expansion of the lattice parameters (Fig. 1) show anisotropic character, at that some deviation from a linearity is observed. Drop of the cell volume is observed at the phase transition. Temperature dependencies of the interatomic distances reflect the structural changes occurred at the phase transition.

Table 2. Refined structural parameters of rhombohedral $La_{0.9}Gd_{0.1}GaO_3$ phase (sp. group *R*-3*c*).

Atom, sites		823 K	873 K	973 K	1073 K	1173 K
	a, Å	5.5354(2)	5.5394(2)	5.5452(2)	5.5503(2)	5.5557(2)
	c, Å	13.4415(8)	13.4484(6)	13.4656(6)	13.4847(6)	13.5063(6)
RE, 6*a* (0 0 ¼)	*B(is/eq)*	1.63(13)	1.45(9)	1.38(10)	1.62(10)	1.72(10)
Ga, 6*b* (0 0 0)	*B(is/eq)*	1.6(2)	1.6(2)	1.4(2)	1.6(2)	1.6(2)
O1, 18*e* (x 0 ¼)	*x*	0.441(6)	0.443(7)	0.430(5)	0.431(5)	0.437(5)
	B(is/eq)	3.0(14)	3.5(16)	2.2(13)	1.7(11)	2.3(13)
	R_I	0.0879	0.0631	0.0782	0.0673	0.0622
	R_P	0.3408	0.2573	0.2275	0.2106	0.2027





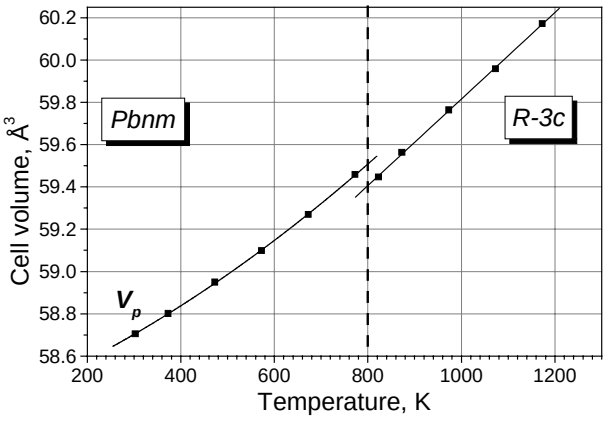


Figure 1**.** Temperature dependencies of the lattice parameters, cell volume and RE–RE interatomic distances in $La_{0.9}Gd_{0.1}GaO_3$ structure. Orthorhombic and rhombohedral lattice parameters were transformed into perovskite pseudo-cell as follow: $a_p=a_o/\sqrt{2}$, $b_p=b_o/\sqrt{2}$, $c_p=c_o/2$, $V_p=V_o/4$; $a_p=a_r/\sqrt{2}$, $c_p=c_r/\sqrt{12}$, $V_p=V_r/6$

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Acknowledgements: *The work was partially supported by WTZ (UKR 01/12), Ukrainian Ministry of Science (Project "Ion") and Polish Committee for Scientific Research (Grant N 7 T08A 00520).*