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Crystal structures and phase transitions of orthorhombic and rhombohedral $RGaO_3$ (R = La, Pr, Nd) investigated by neutron powder diffraction

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Abstract. The rare-earth gallium oxide perovskites $RGaO_3$ (R = La, Pr, Nd) are promising substrates for epitaxy of high-T_c superconductors. In this paper the crystal structures of orthorhombic and rhombohedral $RGaO_3$ have been studied by neutron diffraction, which allows precise localization of light atoms such as oxygen, which are of importance in phase transitions. The lattice parameters, atom positions and tilt angles of the oxygen octahedra were determined in the temperature range 12–1773 K. Lanthanum gallate $LaGaO_3$ shows a phase transition from an orthorhombic phase (*Pbnm*) to a rhombohedral phase (*R3c*) at 425 K. The results are discussed in the classification schemes developed for distorted perovskites.

1. Introduction

Previous investigations of the perovskite-like gallate compounds $RGaO_3$ with distorted and tilted oxygen octahedra were published by Geller [1] and Saine [2]. These investigations, by differential thermal analysis (DTA), high-temperature x-ray powder photography, and infrared and Raman spectroscopy, supplied only information about lattice parameters. Brusset [3] has published the atom parameters and bond lengths of an $NdGaO_3$ single crystal investigated by x-ray diffraction at room temperature. Recently, rare-earth gallates have found applications as substrates for epitaxy of high-T_c superconductors (HTSC) [4, 5]. A small lattice mismatch, similar thermal expansion coefficients, a high thermal and chemical stability, and in particular a small misfit at epitaxial growth temperature, are all important features in growing high-quality HTSC layers. The disadvantage of most perovskites is twinning, caused by structural phase transitions. At substrate polishing the twin boundaries cause surface corrugations, which then lead to a lowering of the critical current density [6]. However, when the $LaGaO_3$ substrates are de-twinned before final polishing, the epitaxial HTSC films can be deposited on flat substrate surfaces [7].

As the first part of systematic neutron scattering measurements of the structures and phase transitions of $RGaO_3$ perovskites (R = La, Pr, Nd) we present here neutron diffraction results in the temperature range 10–1673 K for $LaGaO_3$, and at low temperature and room temperature for $PrGaO_3$ and $NdGaO_3$. Of particular interest is the 424 K phase transition in $LaGaO_3$, where the application of small pressures may suppress domain formation in single crystals. Corresponding studies are in progress.

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Preliminary results concerning $LaGaO_3$ were recently presented [8]. The inelastic neutron measurements used to analyse crystal-field and bulk-magnetic properties of a $NdGaO_3$ powder sample will be published elsewhere [9]. The present structural results will be compared to similarly distorted perovskites.

2. Experimental

Single crystals of $RGaO_3$ were grown in an automatic Czochralski system with a 100 KVARF generator. The starting components R_2O_3 and Ga_2O_3 were molten in Ir crucibles of 40 and 60 mm diameter, and crystals were grown on [100] seed crystals at rates between 1–4 mm h^{-1}. For our investigations the single-crystal fragments were made into powder. All neutron experiments with these polycrystalline $RGaO_3$ (R = La, Pr, Nd) compounds were performed on the multi-detector powder diffractometer DMC [10], at the Saphir reactor of the Paul Scherrer Institute using a neutron wavelength $\lambda \simeq 1.7$ Å. The three different powders were of good single-phase quality. A $LaGaO_3$ sample of 8 g, enclosed in a vanadium container, was also measured in a special vacuum furnace with external watercooling from 300–1373 K. For measurements in the range 1273–1773 K a mirror heater [11] and a powder sample of 2 g kept in a platinum crucible in air were applied. All temperature-dependent diffraction data were recorded by step scanning with $\Delta 2\theta = 0.1°$ and a 2θ range from 3.0°–134.9° and analysed by means of a modified version of the Wiles–Young program [12]. The neutron scattering amplitudes published in [13] were used.

3. Results

3.1. Low- and room-temperature measurements

At room temperature the rare-earth gallates we investigated possess the centrosymmetric space group *Pbnm* (R = La and Pr) or $Pbn2_1$ (R = Nd) without a centre of symmetry. Figure 1(*a*) shows the unit cell of $LaGaO_3$ in the orthorhombic phase: the oxygen ions form slightly distorted and tilted octahedra around the gallium atoms. The unit cell of $NdGaO_3$ is shown in figure 1(*b*).

As typical results we present observed, calculated and difference neutron diffraction patterns of $LaGaO_3$ in the orthorhombic phase at room temperature (figure 2(*a*)) and in the rhombohedral phase at 493 K (figure 2(*b*)).

In table 1 we summarize the results of the neutron diffraction measurements in the high-resolution mode of the three powder samples of $LaGaO_3$, $NdGaO_3$ and $PrGaO_3$ at 12 K and 298 K. In the space group *Pbnm* the rare-earth atom and oxygen O(1) occupy sites (4c) $(x, y, 1/4)$, Ga (4b) $(1/2, 0, 0)$ and O(2) is in the general (8d) (x, y, z) position; in $Pbn2_1$ there are neodymium, gallium and oxygen in general (4a) (x, y, z) positions, whereas the rare earth is fixed on $(x, y, 1/4)$ as in the *Pbnm* space group.

The effective ionic radii of the rare-earth ions R^{3+} with coordination number 12 are (see [14]) La^{3+}: 1.36 Å; Pr^{3+}: 1.30 Å; Nd^{3+}: 1.27 Å. A comparison of the ionic radii (rare-earth contraction) with the volume of the unit cell and the bond angle θ' in $RGaO_3$ shows that with decreasing effective ionic radius the volume and the bond angle θ' are also decreasing, implying that the octahedra are more tilted.

It is well known that in a perovskite ABO_3 the tolerance factor [15]

$$t = \frac{1}{\sqrt{2}} \frac{d_{AO}}{d_{BO}}$$

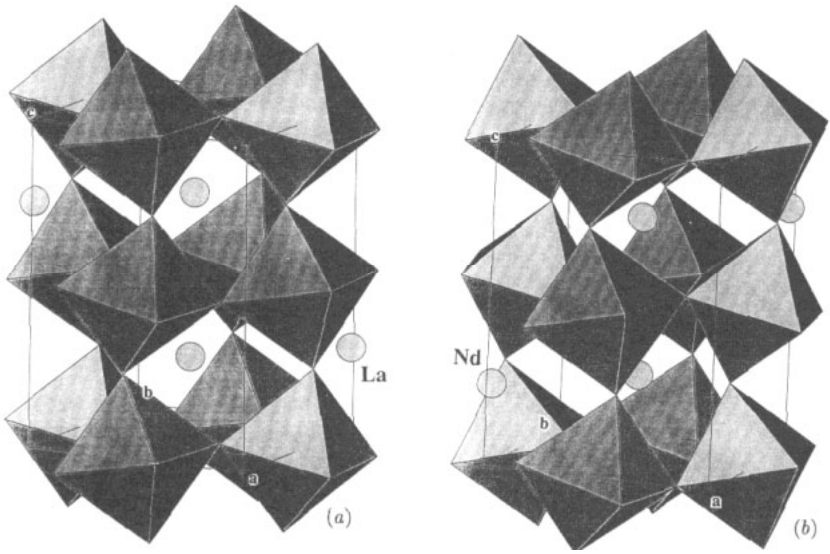

Figure 1. (*a*) The unit cell of $LaGaO_3$ in the orthorhombic phase (*Pbnm*). The oxygen ions form slightly distorted and tilted octahedra around the gallium atoms. (*b*) The unit cell of $NdGaO_3$ in the orthorhombic phase ($Pbn2_1$). The oxygen ions form slightly distorted and tilted octahedra around the gallium atoms.

is a relevant parameter for estimating the degree of distortion. For instance, the orthorhombic distortion increases when t decreases. The values of t in these $RGaO_3$ compounds at room temperature are 0.9483 in $LaGaO_3$, 0.9312 in $PrGaO_3$ and 0.9133 in $NdGaO_3$.

3.2. High-temperature measurements on $LaGaO_3$

We confirmed the low-temperature phase transition and determined the space group and the atom parameters of $LaGaO_3$. In the first phase transition at $T \sim 423$ K [4], $LaGaO_3$ transforms from the orthorhombic *Pbnm* phase to the rhombohedral *R*3c phase, but a second transition at $T \sim 1148$ K [1] could not be confirmed. In figure 3 the unit cell of the rhombohedral phase is shown. In table 2 results of four typical measurements at different temperatures are shown, where the highest temperature was obtained by means of a mirror furnace in air. With an average Ga–O distance of 1.9749 Å and an average La–O distance of 2.7661 Å we have a tolerance factor $t = 0.9904$.

Normally, phase transitions due to distortions are second order in nature. It is possible to get mono-domain single crystals of $LaGaO_3$ by applying uniaxial pressure of a few bars in order to prefer a certain orientation. We can also follow up the phase transition in polarized light since $LaGaO_3$ single crystals are transparent.

4. Discussion

Distorted perovskite structures may be described by three components: the anion octahedra are tilted or rotated, these octahedra are distorted, and the cations are displaced. For perovskite structures without centrosymmetry, usually the cations are displaced, and for *R*3*c*, for example, ferroelectricity is observed. The main component of the distortion from ideal

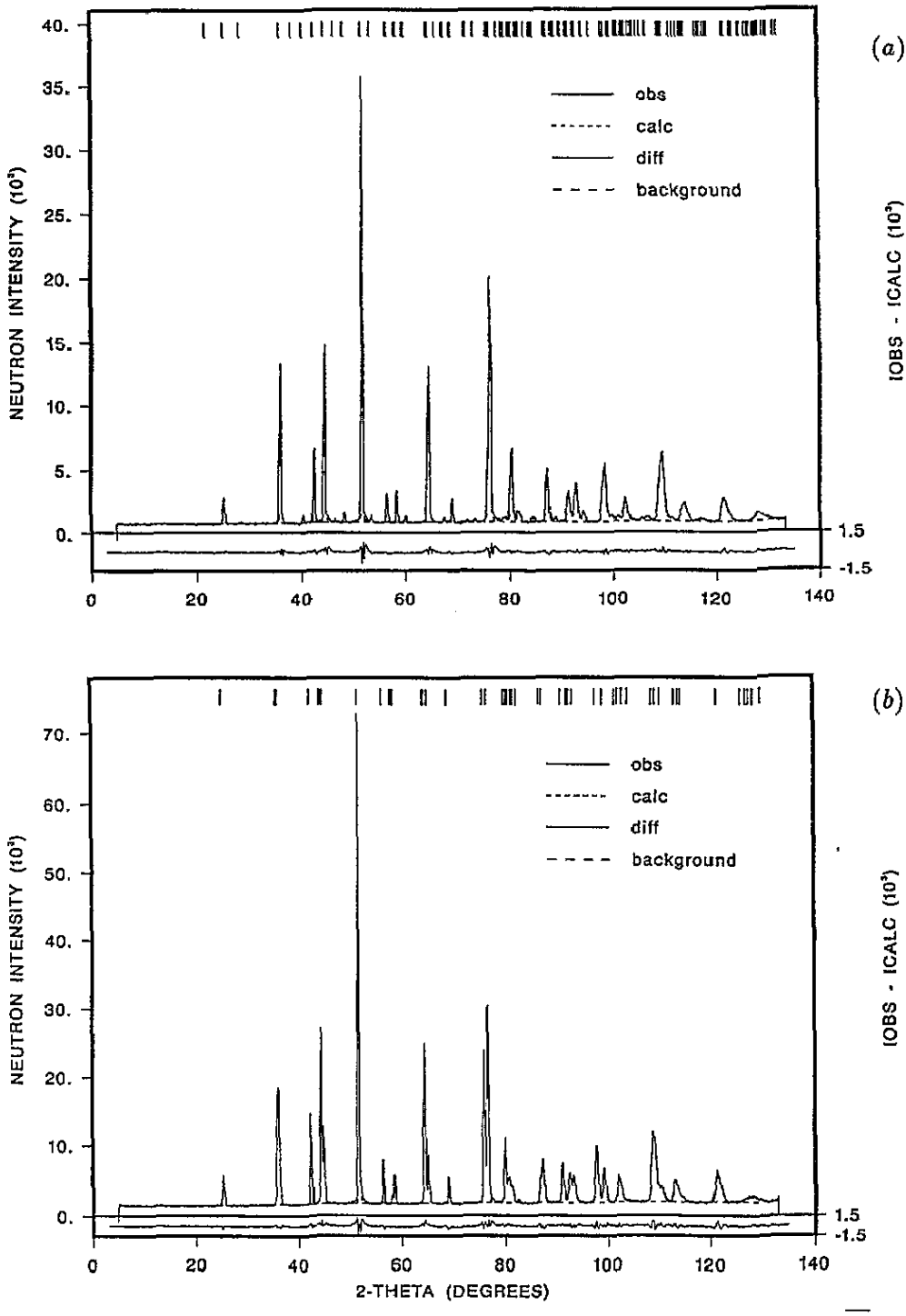

Figure 2. (*a*) Observed, calculated and difference neutron diffraction patterns of $LaGaO_3$ powder sample at 295 K in the orthorhombic phase. (*b*) Observed, calculated and difference neutron diffraction patterns of $LaGaO_3$ powder sample at 493 K in the rhombohedral phase.

Table 1. Refined lattice parameters a, b, c; isotropic temperature factors B and bond angles $\theta' = \text{Ga–O(1)–Ga}$, $\theta'' = \text{Ga–O(2)–Ga}$ and $\theta''' = \text{Ga–O(3)–Ga}$ (all measured in degrees) of the powder samples $RGaO_3$ (R = La, Pr, Nd) at 12 K and 298 K; λ is the neutron wavelength; R_{wp} and R_I are the agreement values concerning weighted profile and integrated intensities, respectively; R_{exp} is the statistically expected value, χ^2 is the accuracy of fit $(= R_{wp}/R_{exp})^2$.

		$LaGaO_3$		$PrGaO_3$		$NdGaO_3$	
T (K)		12	298	12	298	12	298
λ (Å)		1.6995	1.6995	1.6984	1.6984	1.6995	1.6995
Space group		*Pbnm*	*Pbnm*	*Pbnm*	*Pbnm*	$Pbn2_1$	$Pbn2_1$
a (Å)		5.5028(6)	5.5269(3)	5.4526(2)	5.4592(2)	5.4245(2)	5.4333(2)
b (Å)		5.4736(5)	5.4943(3)	5.4947(2)	5.4929(2)	5.5016(2)	5.5036(2)
c (Å)		7.7507(10)	7.7774(4)	7.7121(3)	7.7321(3)	7.7018(3)	7.7157(3)
V (Å^3)		233.45(8)	236.17(4)	231.06(3)	231.86(3)	229.85(3)	230.72(3)
R	x	−0.0021(11)	−0.0030(7)	−0.0065(9)	−0.0066(10)	0.0100(4)	0.0094(4)
	y	−0.0216(6)	−0.0179(5)	−0.0386(4)	−0.0357(5)	0.0434(3)	0.0418(3)
	z	0.25	0.25	0.25	0.25	0.25	0.25
	B (Å^2)	−0.02(4)	0.37(4)	1.90(5)	0.54(5)	−0.22(3)	−0.02(4)
Ga	x	0.5	0.5	0.5	0.5	0.5034(22)	0.5048(19)
	y	0	0	0	0	−0.0040(22)	−0.0044(21)
	z	0	0	0	0	0.5063(8)	0.5068(8)
	B (Å^2)	0.12(4)	0.29(4)	1.50(3)	0.13(3)	0.06(4)	0.13(4)
O(1)	x	0.0709(10)	0.0665(7)	0.0786(5)	0.0769(6)	0.5829(4)	0.5825(5)
	y	0.5056(12)	0.5033(9)	0.5164(4)	0.5152(4)	−0.0187(4)	−0.0178(4)
	z	0.25	0.25	0.25	0.25	0.2660(9)	0.2640(11)
	B (Å^2)	0.25(4)	0.58(4)	1.66(5)	0.28(6)	−0.02(3)	0.17(3)
O(2)	x	−0.2276(8)	−0.2305(6)	−0.2123(3)	−0.2130(3)	0.2874(13)	0.2853(13)
	y	0.2273(8)	0.2289(6)	0.2109(3)	0.2116(3)	0.2881(14)	0.2889(16)
	z	0.0347(4)	0.0354(3)	0.0419(2)	0.0420(3)	0.4668(12)	0.4679(13)
	B (Å^2)	0.25(4)	0.58(4)	1.65(4)	0.30(4)	−0.02(3)	0.17(3)
O(3)	x					0.2963(15)	0.2972(14)
	y					0.2976(15)	0.2953(16)
	z					0.0538(11)	0.0539(12)
	B (Å^2)					−0.02(3)	0.17(3)
θ'		157.2(3)	158.6(2)	154.4(2)	155.0(2)	153.1(1)	153.3(2)
θ''		161.2(2)	161.5(2)	154.4(1)	154.6(1)	154.9(7)	155.3(7)
θ'''						150.5(6)	150.8(7)
R_{wp}	9.29	9.65	8.56	9.29	7.42	7.41	
R_{exp}	1.30	2.60	3.02	2.66	1.92	1.90	
χ^2	4.322	6.044	3.171	4.867	3.978	3.670	
R_I	4.13	3.84	4.25	4.26	3.72	4.01	

cubic structure corresponds to the tilting of the GaO_6 octahedra, which is in the orthorhombic phase of the $a^0b^+c^+$ type. This means that tilts only occur around b and c orthorhombic axes. The positive signs mean that b and c tilts are in phase when successive octahedra

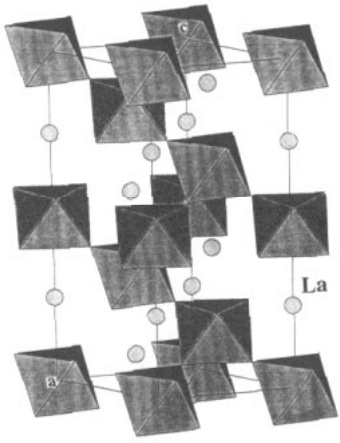

Figure 3. The unit cell of $LaGaO_3$ in the rhombohedral phase ($R3c$). The oxygen ions form slightly distorted and tilted octahedra around the gallium atoms.

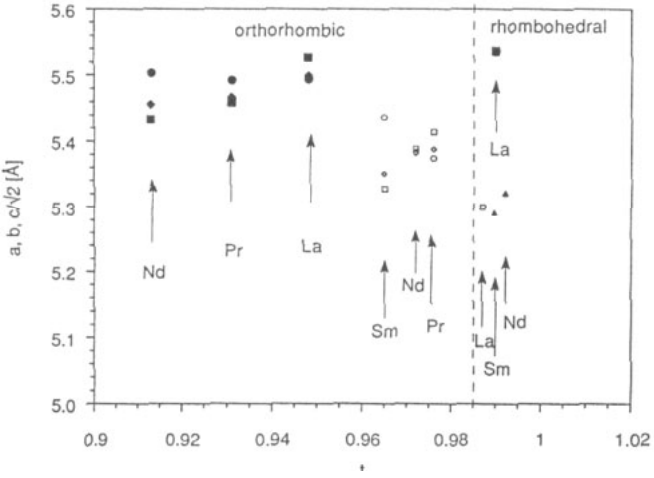

Figure 4. Tolerance factor dependence of lattice parameters a, b and $c/\sqrt{2}$ of some perovskites ABO_3. It shows the boundary between orthorhombic and rhombohedral structures near $t = 0.985$. In the case of the orthorhombic structure the meaning of the dots is as follows. ■: a; ●: b; ♦: $c/\sqrt{2}$ for $RGaO_3$ (R = La, Pr, Nd), and □: a; ○: b; ◇: $c/\sqrt{2}$ for $RNiO_3$ (R = Pr, Nd, Sm). In the rhombohedral structure the meaning of the dots is as follows. ■: a for $LaGaO_3$, □: a for $LaNiO_3$ and ▲: a for $RAlO_3$ (R = Nd, Sm).

along the same axis are considered. In the terminology of Glazer [16] the distortion is of $a^-b^-c^+$ pseudocubic type. The rhombohedral phase $R3c$ implies a three-tilt system, with the symbol $a^-a^-a^-$ when we refer to the rhombohedral axes.

Another systematic description of the atom parameters in rhombohedral perovskites was established by Megaw [17]; the Megaw distortion parameters are the following: La $(0, 0, 1/4 + s - t)$, Ga $(0, 0, 0)$, and O $(1/6 - 2e - 2d, 1/3 - 4d, 1/12 - t)$ with the tilt

Table 2. High-temperature results on $LaGaO_3$. At 413 K, below the phase transition temperature, $LaGaO_3$ crystallizes in an orthorhombic structure corresponding to space group *Pbnm*, and changes above 425 K to the rhombohedral structure of symmetry *R3c*. The highest temperature at 1673 K was measured in a mirror furnace in air. θ' = Ga–O(1)–Ga; θ'' = Ga–O(2)–Ga.

T (K)		413	573	1353	1673
Space group		*Pbnm*	*R3c*	*R3c*	*R3c*
a (Å)		5.5295(7)	5.5388(3)	5.5835(4)	5.6118(14)
b (Å)		5.4949(6)			
c (Å)		7.7850(11)	13.4090(9)	13.6016(4)	13.7472(45)
V (Å^3)		236.54(9)	356.25(7)	367.23(6)	374.93(31)
La	x	−0.0020(13)	0	0	0
	y	−0.0151(8)	0	0	0
	z	0.25	0.2507(12)	0.2507(14)	0.2422(15)
	B (Å^2)	0.55(6)	0.63(7)	1.87(10)	3.71(29)
Ga	x	0.5	0	0	0
	y	0	0	0	0
	z	0	0	0	0
	B (Å^2)	0.31(5)	0.41(6)	1.19(8)	2.27(28)
O(1)	x	0.0672(15)	0.1158(9)	0.1245(12)	0.2412(28)
	y	0.5007(17)	0.3426(16)	0.3439(21)	0.3905(33)
	z	0.25	0.0775(11)	0.0725(13)	0.0296(18)
	B (Å^2)	0.75(5)	0.93(4)	2.45(7)	3.8(19)
O(2)	x	−0.2327(10)			
	y	0.2322(11)			
	z	0.0355(6)			
	B (Å^2)	0.75(5)			
θ'		158.4(5)	161.4(5)	162.4(7)	135.6(11)
θ''		162.0(3)			
R_{exp}		1.08	1.33	2.63	2.88
R_{wp}		8.37	7.92	10.71	23.45
χ^2		18.95	10.22	3.292	9.599
R_I		4.23	2.88	4.10	16.10

angle $\omega = \tan^{-1}(4e\sqrt{3})$. In the ideal perovskite these parameters are equal to zero. For rhombohedral $LaGaO_3$ the temperature dependence of the Megaw distortion parameters are shown in table 3.

The gallates are more distorted than other perovskites, such as nickelates or aluminates. In figure 4 we show the dependence on the tolerance factor t of the lattice parameters a, b, $c\sqrt{2}$ of $RGaO_3$ compounds, and orthorhombic or rhombohedral structures of $RNiO_3$ [18] and $RAlO_3$ [19] with the boundary between these two phases near $t = 0.985$ [18]. The behaviour of $LaGaO_3$ is also well matched.

From these results the expansion coefficients of $LaGaO_3$ are calculated for the temperature ranges 12–413 K (orthorhombic) and 573–1353 K (rhombohedral). In figures 5(*a*) and 5(*b*) the temperature dependence of the lattice parameters for the rhombohedral phase (as a and c of the hexagonal cell) are shown for the temperature

Table 4. Expansion coefficients α_a, α_b, α_c and α_V (in $10^{-6}K^{-1}$) of $LaGaO_3$ in the orthorhombic phase (temperature range 12–413 K) and in the rhombohedral phase (573–1353 K).

Space group	T (K)	α_a	α_b	α_c	α_V
Pbnm	12–413	12.1(5)	9.7(4)	11.0(5)	33.0(4)
R3c	573–1353	10.3(2)		18.4(3)	39.5(5)

range 428–1353 K.

The expansion coefficients are defined as follows:

$$\alpha_x = \frac{\Delta x}{x \Delta T} \qquad x = a, b, c, V$$

with the margin of error of the expansion coefficients $\delta\alpha_x$:

$$\delta\alpha_x = \frac{1}{x\Delta T}\left[\delta(\Delta x) + \Delta x\left(\frac{\delta x}{x} + \frac{\delta(\Delta T)}{\Delta T}\right)\right]$$

with $\delta(\Delta T) = 5\,\mathrm{K}$.

The resulting expansion coefficients are summarized in table 4.

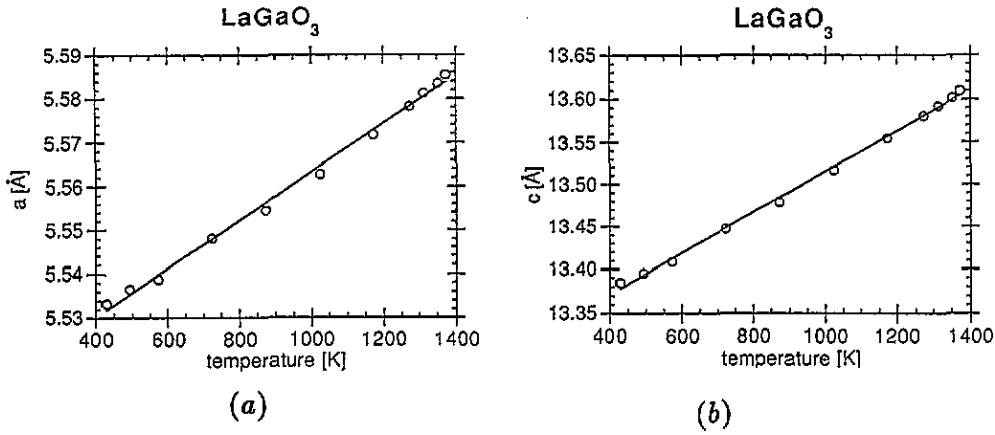

Figure 5. (*a*) Temperature dependence of the hexagonal lattice parameter a of $LaGaO_3$ in the rhombohedral phase from 400–1400 K. (*b*) Temperature dependence of the hexagonal lattice parameter c of $LaGaO_3$ in the rhombohedral phase from 400–1400 K.

Table 3. Temperature dependences of the distortion parameters and bond angles of rhombohedral $LaGaO_3$ in the Megaw description.

T (K)	s	t	d	e	w (deg)
573	0.0065(12)	0.0058(11)	−0.0023(4)	0.0278(5)	10.9(2)
1353	0.0115(14)	0.0108(13)	−0.0026(5)	0.0237(6)	9.3(3)
1673	0.0459(15)	0.0537(18)	−0.0143(8)	−0.0299(14)	−11.7(5)

5. Summary

The structures of high-quality powders of $LaGaO_3$, $NdGaO_3$ and $PrGaO_3$ have been refined from neutron diffraction data taken at low (12 K) and ambient temperatures. Also, for $LaGaO_3$, high-temperature data (up to 1673 K) were refined, the phase transition from *Pbnm* to *R3c* at 150 K confirmed, and thermal expansion coefficients derived. Compared to similar nickelates and aluminates, the gallates appear to be more distorted, but otherwise fit well into the general scheme of distorted perovskites.

Acknowledgments

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References

[1] Geller S 1957 *Acta Crystallogr.* **10** 243
Geller S, Curlander P J and Ruse G F 1974 *Mater. Res. Bull.* **9** 637
[2] Saine M C 1982 *Spectrochim. Acta* A **38** 19–24
O'Bryan H M, Gallagher P K, Berkstresser G W and Brandle C D 1990 *J. Mater. Res.* **5** 183
[3] Brusset H 1967 *Bull. Soc. Chem. France* **8** 2886–90
[4] Sandstrom R L, Giess E A, Gallagher W J, Segmüller A, Cooper E I, Chisholm M F, Gupta A, Shinde S and Laibowitz R B 1988 *Appl. Phys. Lett.* **53** 1874
[5] Scheel H J, Berkowski M and Chabot B 1991 *J. Cryst. Growth* **115** 19
[6] Miyazawa S 1989 *Appl. Phys. Lett.* **55** 2230
[7] Berkowski M, Maamouri M and Scheel H J 1993 in preparation
[8] Marti W, Fischer P, Furrer A, Scheel H J and Fadin M *13th General Conf. of the Condensed Matter Division of the European Physical Society (Regensburg, 1993)*
[9] Podlesnyak A 1993 *J. Phys.: Condens. Matter* **5** 8973
[10] Schefer J, Fischer P, Heer H, Isacson A, Koch M and Thut R 1990 *Nucl. Instrum. Methods* A **288** 477
[11] Lorenz G, Neder R B, Marxreiter J, Frey F and Schneider J 1993 *J. Appl. Crystallogr.* **26** at press
[12] Wiles D B and Young R A 1981 *J. Appl. Crystallogr.* **14** 151
[13] Sears V F 1993 *Neutron News* **3** 26
[14] Shannon R D 1976 *Acta Crystallogr.* A **32** 751
[15] Goodenough J B and Longo J M 1970 *Magnetic and Other Properties and Related Compounds* ed K H Hellwege and A M Hellwege (Berlin: Springer) ch 3, p 126
[16] Glazer A M 1975 *Acta Crystallogr.* A **31** 756
[17] Megaw H D and Darlington C N W 1975 *Acta Crystallogr.* A **31** 161
[18] Lacorre P, Pannetier J, Nazzal A I, Wang P W and Huang F C 1991 *J. Solid State Chem.* **91** 225
[19] Marezio M, Dernier P D and Remeika J P 1972 *J. Solid State Chem.* **4** 11–9