Pressure-induced orthorhombic to rhombohedral phase transition in $LaGaO_3$

LETTER TO THE EDITOR

Pressure-induced orthorhombic to rhombohedral phase transition in LaGaO$_3$

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Abstract
The influence of pressure on the crystal structure of LaGaO$_3$ has been studied
using synchrotron x-ray diffraction. At atmospheric pressure LaGaO$_3$ has an
orthorhombic structure in *Pnma* and undergoes a first-order phase transition
to a rhombohedral structure near 2.5 GPa. The transition is reversible and the
orthorhombic structure is recovered upon releasing the pressure below 2 GPa.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

The perovskite lanthanum gallate (LaGaO$_3$) has lattice spacings that make it a good substrate
for high-T_c superconductors (HTSC) and colossal magnetoresistive (CMR) film epitaxy [1–3].
Interest in this compound has been further fuelled by its promising behaviour as an electrolyte
for solid state fuel cells [4–6]. For both applications it is typical to partially substitute for La
and/or Ga in order to enhance its desirable properties.

Pure LaGaO$_3$ has an orthorhombic (*Pnma*) perovskite structure under ambient conditions
and undergoes a first-order phase transition to a rhombohedral structure in $R\overline{3}c$ near
150 °C [7, 8]. These two structures differ with respect to the tilts of the GaO$_6$ octahedra.
A description of the tilts in ABO$_3$ type perovskites has been given by Glazer [9] and the
relationships between the possible tilt systems have recently been expanded upon by Howard
and Stokes [10]. The *Pnma* to $R\overline{3}c$ transition in LaGaO$_3$ is sensitive to chemical substitution,
and partially replacing the La with a smaller lanthanide ion such as Nd or Sm stabilizes the
orthorhombic structure [11, 12]. The smaller lanthanide tends to increase the magnitude of
the tilts of the octahedra. It is not surprising therefore that the temperature of the transition
to the rhombohedral structure has been found to increase with Ln content in the three series
La$_{1-x}$Ln$_x$GaO$_3$ Ln = Pr, Nd or Sm [11, 12]. There is now a considerable body of evidence
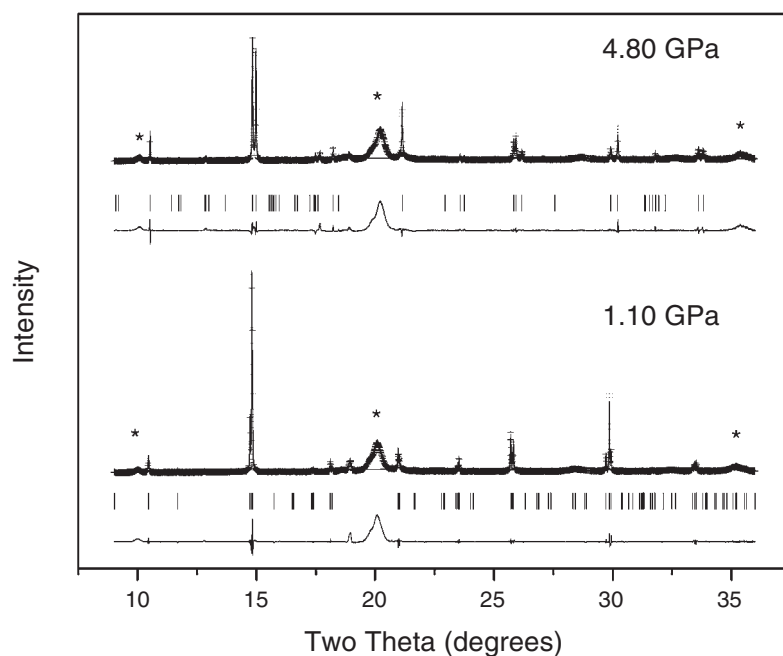
Figure 1. Observed and calculated room temperature x-ray powder diffraction profiles for LaGaO$_3$ at 1.10 and 4.80 GPa. The short vertical bars mark the positions of the allowed Bragg reflections. The broad feature near 20° is due to the gasket (marked with *) and was excluded from the calculation.

demonstrating that the tilts of the BO$_6$ octahedra are reduced with increasing temperature, and in numerous examples this leads to a sequence of phase transitions where the archetypal cubic ($Pm3m$) structure is ultimately obtained [13–18].

Pressure can be viewed as the third method of controlling the relative stability of the orthorhombic and rhombohedral phases. To a rough approximation the effect of pressure is expected to represent the inverse of temperature (increasing the pressure should reduce the volume of the cell as will reducing the temperature) and it can be postulated that phase transitions that occur upon cooling might be observed upon application of external pressure [19]. This was recently observed in another perovskite, PrAlO$_3$ [20]. This relationship between temperature and pressure assumes that the volume change at the phase transition is negligible, and the precise relationship between pressure and temperature has yet to be established. For LaGaO$_3$ the volume of the high-temperature rhombohedral phase is measurably smaller than that of the low-temperature orthorhombic phase [8] and the reverse might be expected, that is application of pressure may stabilize the rhombohedral phase at room temperature. Here we describe high-resolution x-ray diffraction studies of LaGaO$_3$ at pressures of up to 4.8 GPa aimed at examining this possibility.

2. Experiment

The polycrystalline sample of LaGaO$_3$ was prepared by the solid state reaction of stoichiometric amounts of La$_2$O$_3$ and Ga$_2$O$_3$ at 1173 K in air for 24 h and then, with periodic regrinding, at 1373 K for 48 h and 1623 K for 24 h. A modified Merrill–Bassett diamond-anvil cell was used for the x-ray studies in the pressure range 0.0–4.8 GPa. The powdered sample together
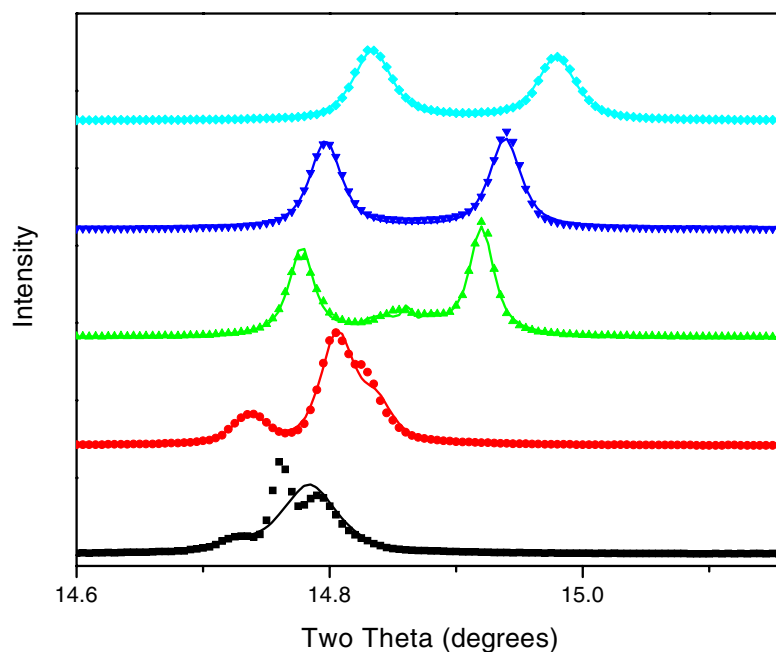
Figure 2. Pressure-induced evolution of a portion of the x-ray diffraction patterns for LaGaO$_3$ showing the conversion of the 020/112/200 triplet of the orthorhombic phase to the 110/014 doublet of the rhombohedral phase. The sharp peak near 14.75° in the pattern at 0.32 GPa is from a ruby. The pressures are, from the bottom 0.32, 1.10, 2.45, 3.08 and 4.80 GPa.

with a few small ruby chips was loaded into a 200 μm hole in a steel gasket. A methanol–ethanol–water (16:3:1) mixture was used as the hydrostatic pressure transmitting medium. The pressure was calibrated by measuring the shift of the R$_1$ fluorescence line of ruby before and after each run. The x-ray diffraction data were collected using synchrotron radiation at the bending magnet beamline, X7A, of the National Synchrotron Light Source at Brookhaven National Laboratory. A wavelength of 0.7054 Å was selected using a bent Si 220 focusing crystal monochromator. Data were collected using a linear position-sensitive detector mounted about 450 mm from the sample. Further information on the configuration of the instrument and the data collection procedure can be found elsewhere [21]. The program RIETICA was employed to refine the lattice parameters using intensities extracted by the LaBail method [22].

3. Results and discussion

The ambient pressure diffraction pattern of LaGaO$_3$ at room temperature showed only reflections due to the perovskite-like phase. All observed reflections could be indexed on the basis of an orthorhombic cell with $a = 5.5094(3)$, $b = 5.4786(3)$ and $c = 7.7532(5)$ Å. We were not able to refine the structure in the orthorhombic phase once the sample had been introduced into the diamond-anvil cell, presumably due to a combination of effects including preferred orientation, the limited 2θ angular range and overlap with extraneous peaks from the gasket and/or ruby. Nevertheless a LaBail type analysis proved straightforward and an example is shown in figure 1.

Figure 2 shows a portion of the x-ray diffraction patterns at room temperature collected with successively higher pressures. In orthorhombic *Pnma* symmetry the cubic 110 reflection
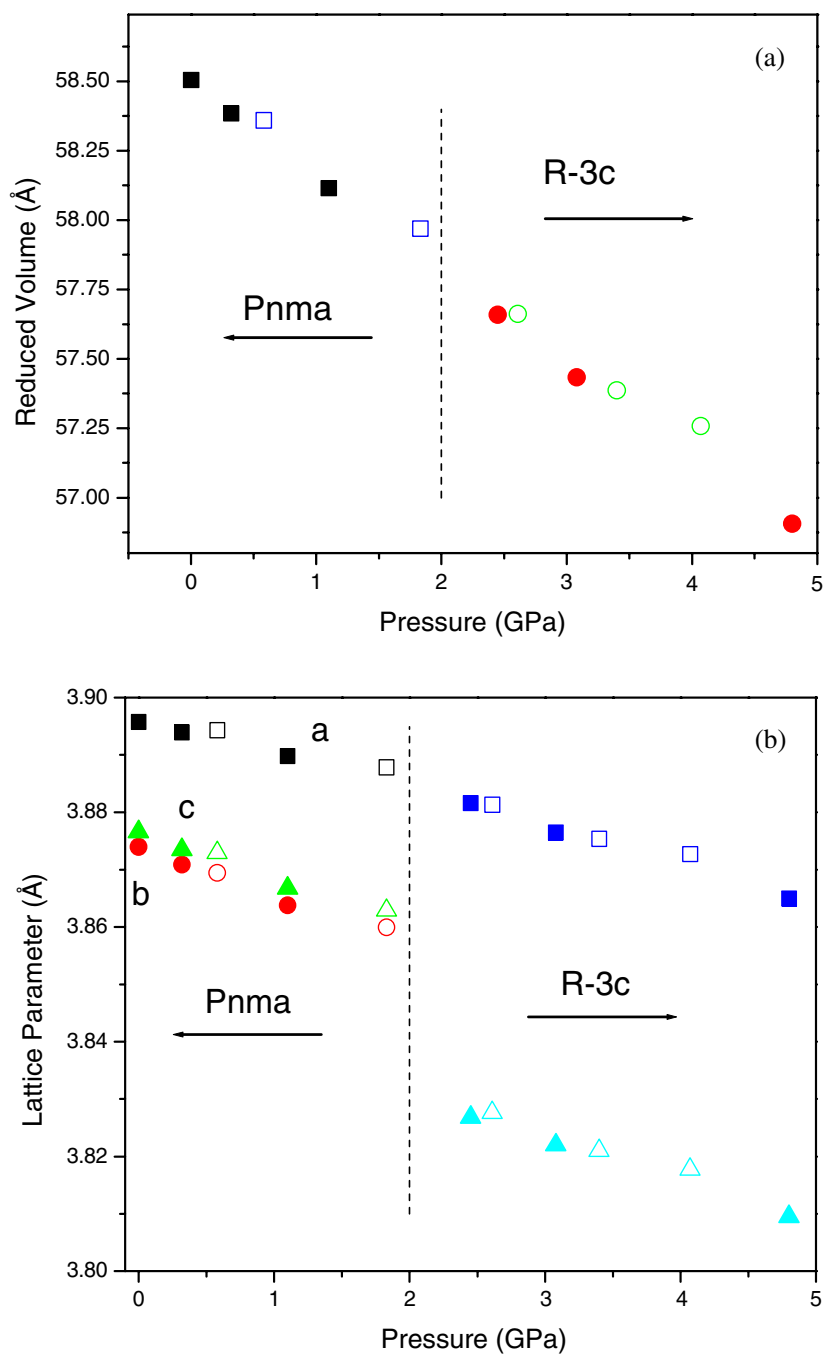
Figure 3. (a) Variation of the volume of LaGaO$_3$ and (b) of the lattice parameters with pressure. The open symbols were for samples studied with successively higher pressure and the closed symbols were collected as the pressure was progressively lowered from 4.8 GPa. The vertical line shows the approximate position of the orthorhombic to rhombohedral phase transition. In both cells the lattice parameters have been reduced to their equivalent cubic values.

is split into a triplet (the 020, 112 and 200 reflections) while in rhombohedral symmetry it appears as a doublet from the 110 and 014 reflections. Examination of the region of the diffraction pattern that includes these reflections shows that below 1.1 GPa the diffraction pattern consists of a triplet indicative of orthorhombic symmetry. Unfortunately the pattern at 0.3 GPa contains an additional reflection from the ruby, which also falls in this area. With increasing pressure the volume of the cell contracts (figure 3), and the peaks move to successively higher angles(figure 2). At 2.5 GPa the pattern in this region is essentially a doublet indicative of rhombohedral symmetry although some additional intensity is evident near $2\theta = 14.85°$ between the rhombohedral 110 and 014 reflections, demonstrating that some residual orthorhombic phase persists. The existence of an extensive two-phase region has been noted in studies of the thermally induced transition in some substituted analogues of the type $La_{1-x}Ln_xGaO_3$, Ln = Sm, Pr, Nd [11, 12]. Above 2.5 GPa the pattern contains a simple doublet in this region, and as demonstrated in figure 1 the observed pattern is well reproduced in $R\bar{3}c$, this being the space group observed in $LaGaO_3$ in recent high-temperature powder neutron diffraction studies [7, 23].

Releasing the pressure reversed the transition with the pattern recorded at 1.83 GPa consisting predominantly of the orthorhombic phase together with a small amount of the rhombohedral phase. At pressures below this the pattern showed evidence for only the orthorhombic phase. Surprisingly there is very little hysteresis in the observed volume (figure 3), and upon total release the observed volume was very similar to that found for $LaGaO_3$ at room temperature.

The crystal structure of $LaGaO_3$ is on the border between the rhombohedral and orthorhombic structures. Transitions between these can be induced by increasing either the temperature or pressure or by adding strain to the lattice by chemical substitution. Obviously this is undesirable if $LaGaO_3$ is to be employed as a support for HTSC or CMR materials, although we are unaware of any studies where the structural phase transition has been shown to be a factor in a device. It is clear that chemical substitutions can increase the transition temperature, and it remains to be determined if these too increase the pressure needed to induce the transition to the rhombohedral structure. Determining the precise relationship between temperature and pressure in phase transitions of these types is an obvious priority.

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