

EXPLORATION OF HIGH PRESSURE PHASE IN LaGaO₃ AND LaCrO₃

T. Shibasaki¹, T. Furuya¹, J. Kuwahara², Y. Takahashi², H. Takahashi¹ and T. Hashimoto^{1*}

¹Department of Integrated Sciences in Physics and Biology, College of Humanities and Sciences, Nihon University, 3-25-40 Sakurajousui, Setagaya-ku, Tokyo 156-8550, Japan

²Department of Applied Chemistry, Faculty of Science and Engineering, Chuo University, 1-13-27 Kasuga, Bunkyo-ku, Tokyo 112-8551, Japan

Structural phase transitions upon the application of high pressure in LaGaO₃ and LaCrO₃, which were prospected from diffraction and thermal analyses of phase transition under ambient pressure, were discovered by using high-pressure X-ray diffraction. It was revealed that the crystal structures of LaCrO₃ and LaGaO₃ changed completely from that of orthorhombic distorted perovskite to that of a rhombohedral distorted one upon the application of pressure higher than 5.4 and 3.0 GPa, respectively, at room temperature. The variation of lattice constants with pressure was investigated for the high-pressure rhombohedral phases of LaCrO₃ and LaGaO₃ and isothermal compressibility was estimated. The variation of lattice constants with pressure at room temperature in the high-pressure rhombohedral phase was compared with that with temperature at ambient pressure in high-temperature rhombohedral phase. It was found that the application of pressure decreased the crystal symmetry, which was opposite to the result in the case of increasing the temperature.

Keywords: isothermal compressibility, LaCrO₃, LaGaO₃, phase transition, X-ray diffraction under high pressure

Introduction

As a method of investigating new properties of materials, the application of high pressure has often been reported. The transition temperature of superconducting oxide can be controlled by applying pressure [1]. It has also been reported that the application of pressure affects the thermoelectric property of Ni(S_{1-x}Se_x)₂. [2] From the viewpoint of not only the elucidation of new functions in materials but also application to practical devices, information on the properties, structure and phase transition of materials under high pressure is important. For example, materials employed in solid oxide fuel cells are exposed to not only high temperature but also high pressure due to shear stress originating from the mismatch of thermal expansion between materials.

At present, few papers which include the theoretical prediction of phase transitions upon the application of pressure are available. One of the authors predicted pressure-induced structural phase transition in LaCrO₃ by considering the behavior of structural phase transition at high temperature at ambient pressure [3]. Figure 1 summarizes the proposed phase diagram of LaCrO₃. The crystal structure of LaCrO₃ is that of orthorhombic distorted GdFeO₃-type perovskite with the lattice constant of $\sim\sqrt{2}a_p x \sim\sqrt{2}a_p x \sim 2a_p$, where a_p is the lattice constant of a pseudocubic perovskite structure at room temperature at 1 atm [4]. The first-order

structural phase transition was observed at about 260°C at 1 atm by differential scanning calorimetry [5, 6], X-ray diffraction at high temperature [6, 7] and dilatometry [8]. The crystal structure changes from that of orthorhombic to rhombohedral distorted LaAlO₃-type perovskite at the phase transition, which involves the absorption of heat and a decrease of volume. The pressure, P , and temperature, T , at the first-order phase transition should satisfy the Clapeyron formula described below.

$$dP/dT = \Delta H / (T\Delta V)$$

where ΔH and ΔV represent the variations of enthalpy and molar volume at the phase transition, respectively [9]. Since dP/dT is negative due to positive ΔH and negative ΔV at the phase transition of LaCrO₃, the crystal

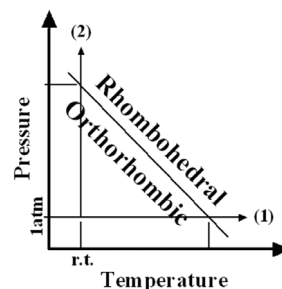


Fig. 1 Proposed phase diagram of LaCrO₃ and LaGaO₃. Phase transitions with increase of temperature and pressure are depicted by arrows (1) and (2), respectively

* Author for correspondence: takuya@chs.nihon-u.ac.jp

system was expected to become rhombohedral upon the application of pressure even at room temperature as Fig. 1 shows.

One of the authors carried out X-ray diffraction measurement of LaCrO_3 under high pressures at room temperature and confirmed that the crystal structure of LaCrO_3 changed completely from orthorhombic to rhombohedral under the pressure of 5.5 GPa. This is in qualitative agreement with the expected phase diagram, although a lower transition pressure was expected from the Clapeyron formula [3]. However, it was not clarified whether this guiding principle using the Clapeyron formula is applicable to other materials. Kennedy *et al.* discovered a pressure-induced structural phase transition of LaGaO_3 from orthorhombic distorted perovskite to a rhombohedral one at around 2.5 GPa [10]. However, they did not employ the thermodynamic consideration as a guiding principle for the discovery of this pressure-induced phase transition. In addition, their analyses of crystal structure under various pressures were not definitive since fairly large X-ray diffraction peaks originating from the experimental apparatus were observed in their study. In our study, a phase transition of LaGaO_3 induced by pressure was thermodynamically predicted since it shows a phase transition similar to that of LaCrO_3 at about 120°C at ambient pressure [11, 12] and it was confirmed by using a superior diffraction apparatus. In addition, the dependence of lattice constants on pressure and the compressibility of high-pressure phases of LaCrO_3 and LaGaO_3 were measured and the characteristics of the high-pressure phase at room temperature were compared with those of the high-temperature phase at 1 atm.

Experimental

LaCrO_3 polycrystalline powder was prepared by the Pechini method using $\text{La}(\text{NO}_3)_3$ and $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ as raw materials. LaGaO_3 powder was prepared by the conventional solid-state reaction method. Each method has been described in detail in separate papers [13, 14]. Both specimens were confirmed to be almost the single phase of orthorhombic distorted perovskite by X-ray diffraction measurement using Rigaku RINT-2500 ($\text{CuK}\alpha$: 50 kV, 250 mA).

In order to estimate ΔH at the phase transition of LaGaO_3 , power-compensated differential scanning calorimetry (DSC) was carried out using Pyris-1 (Perkin-Elmer Co., Ltd.) with N_2 flow of 20 ml min^{-1} . The LaGaO_3 powder was crimped in an Al pan. Al_2O_3 powder crimped in an Al cell was used as reference. In order to detect the thermal anomaly due to the phase transition, DSC was carried out at a heating rate of 15 K min^{-1} . To estimate the specific heat capacity,

C_p , the 'enthalpy method' was employed for DSC measurement at 10 K intervals. Details of the 'enthalpy method' are presented in a separate paper [15].

For the measurement of ΔV at the phase transition, high-temperature X-ray diffraction patterns of LaGaO_3 were measured at 1 atm. From the Bragg angle of specific diffraction peaks, variations of lattice constants and molar volume with temperature were calculated, as described in detail in a separate paper [14].

A gasketed diamond anvil cell was employed for X-ray diffraction at a pressure of 0.0–10.0 GPa at room temperature. The diamond cell consists of a pair of diamond anvils with a culet of 0.4 mm diameter and a stainless-steel gasket with a 0.15 mm hole serving as the sample chamber. As the pressure medium, a 4:1 methanol:ethanol mixture was used. The LaCrO_3 or LaGaO_3 sample powder was loaded together with a tiny ruby chip and pressure was determined by the ruby fluorescence technique [16]. X-ray diffraction data under various pressures were collected using synchrotron radiation at BL10XU at SPring-8. The wavelength of radiation and the distance between the sample and the imaging plate were determined from the diffraction pattern of CeO_2 . The lattice constants under various pressures were estimated from 2θ values of particular Bragg peaks.

Results and discussion

Thermodynamical prediction of phase transition pressure at room temperature

In the preceding work, the temperature, ΔH and ΔV of LaCrO_3 at the phase transition at 1 atm was reported to be 509 K, 310 J mol^{-1} and $-0.323 \text{ cm}^3 \text{ mol}^{-1}$, respec-

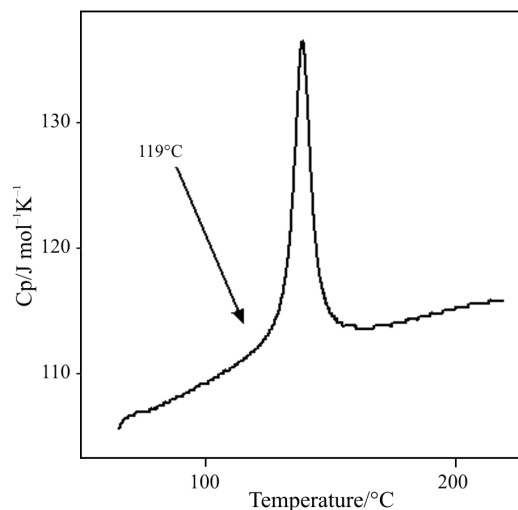


Fig. 2 Specific heat capacity of LaGaO_3 measured by DSC at 1 atm. An endothermic peak attributed to the structural phase transition was observed at 119°C

tively [3]. Figure 2 shows C_p of LaGaO₃ measured by DSC. At 119°C, a peak corresponding to the phase transition upon the absorption of heat was observed, showing agreement with the results of preceding studies [11, 12]. ΔH calculated from the peak area was 250 J mol⁻¹. Figure 3 depicts the variation of the molar volume of LaGaO₃ with temperature at 1 atm measured

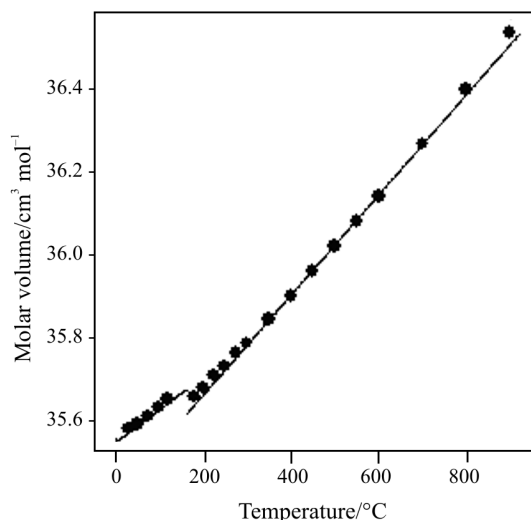


Fig. 3 Temperature dependence of molar volume of LaGaO₃ at 1 atm. Decrease of volume corresponding to the structural phase transition was observed

from high-temperature X-ray diffraction. Details of the calculation method are described in a separate paper [14]. At the phase transition temperature of about 120°C, ΔV of $-0.083 \text{ cm}^3 \text{ mol}^{-1}$ was observed.

Assuming ΔH and ΔV to be independent of pressure since the two phases are solids, the Clapeyron formula can be expressed as

$$dP/dT = -9.59 \cdot 10^8 / T \quad \text{and} \quad dP/dT = -3.01 \cdot 10^9 / T$$

for LaCrO₃ and LaGaO₃, respectively. The following formulas can be obtained by integrating the equation, considering the phase transition temperature at 1 atm:

$$P - 1.01 \cdot 10^5 = -9.59 \cdot 10^8 \ln(T/509) \quad \text{and}$$

$P - 1.01 \cdot 10^5 = -3.01 \cdot 10^9 \ln(T/392)$ for LaCrO₃ and LaGaO₃, respectively. At 293 K, P can be estimated to be 0.53 GPa for LaCrO₃ and 0.83 GPa for LaGaO₃.

Phase transition by application of pressure in LaCrO₃ and LaGaO₃ at room temperature

Figure 4 shows X-ray diffraction patterns of (a) LaCrO₃ and (b) LaGaO₃ at room temperature under various pressures. Almost all the diffraction peaks of LaCrO₃ at 0.8 GPa can be indexed to orthorhombic symmetry with $a=5.460 \text{ \AA}$, $b=5.497 \text{ \AA}$ and $c=7.725 \text{ \AA}$. Variation of the diffraction pattern was observed with increasing pressure up to 8.4 GPa. Diffraction peaks of LaCrO₃ at 8.4 GPa could be indexed assuming hexagonal symmetry with $a=5.437 \text{ \AA}$ and $c=13.061 \text{ \AA}$; this

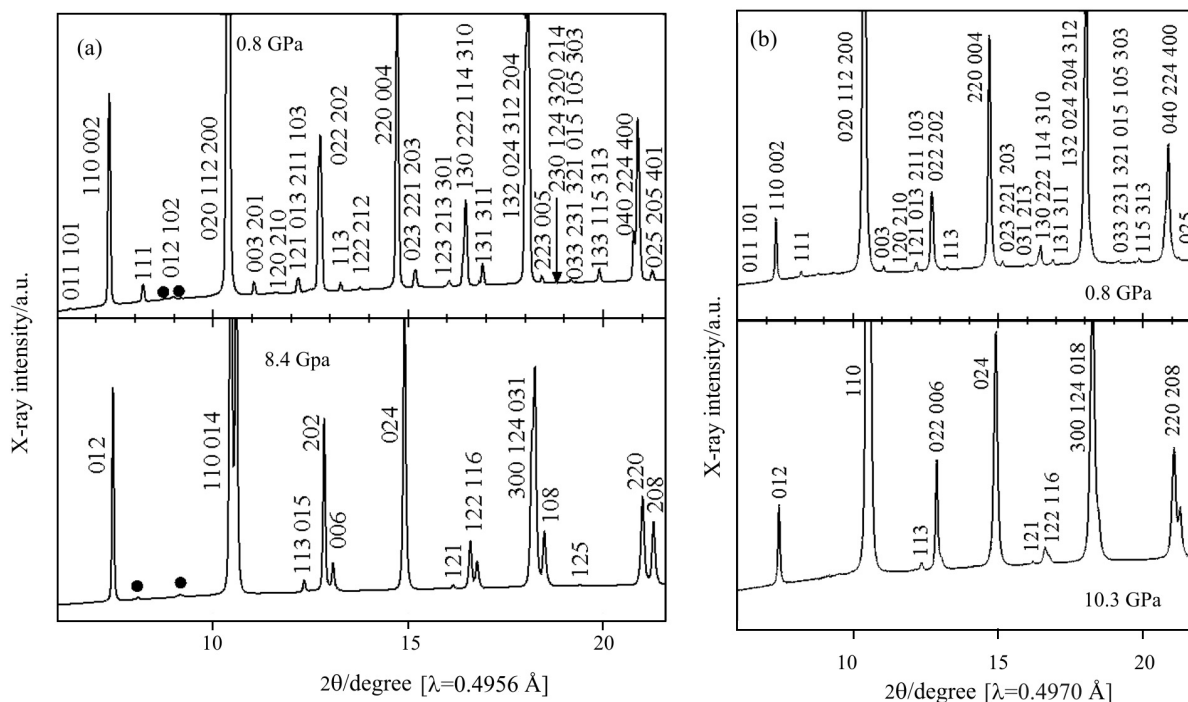


Fig. 4 X-ray diffraction patterns of a – LaCrO₃ and b – LaGaO₃ under various pressures. Diffraction peaks of LaCrO₃ and LaGaO₃ at 0.8 GPa can be indexed to orthorhombic symmetry. Peaks of LaCrO₃ at 8.4 GPa and LaGaO₃ at 10.3 GPa can be assigned to hexagonal symmetry. The hexagonal description could be transformed to the rhombohedral description. Peaks represented by ● can be ascribed to impurities

indicates phase transition upon the application of pressure. This hexagonal symmetry could be transformed to the rhombohedral one since all Miller indices of hexagonal description, hkl , could be transformed to Miller indices of the rhombohedral lattice, $h_R k_R l_R$ according to the following formula: $h_R = (h - k + l)/3$, $k_R = (h + 2k + l)/3$ and $l_R = (-2h - k + l)/3$. The same variation of crystal structure upon the application of pressure was also observed in LaGaO_3 . The X-ray diffraction pattern of LaGaO_3 at a pressure of 0.8 GPa could be indexed to orthorhombic symmetry with $a = 5.476 \text{ \AA}$, $b = 5.516 \text{ \AA}$ and $c = 7.752 \text{ \AA}$. The application of a pressure of 10.3 GPa changed the crystal system to hexagonal with $a = 5.438 \text{ \AA}$ and $c = 13.124 \text{ \AA}$, which could also be transformed to rhombohedral symmetry.

Figure 5 shows X-ray diffraction peaks of LaCrO_3 at room temperature under various pressures. Using an X-ray with a wavelength of 0.4956 \AA , doublet peaks with Miller indices of 022 and 202 should be observed in the 2θ range of $12.3 \sim 13.2^\circ$ for orthorhombic symmetry. For hexagonal, i.e., rhombohedral symmetry, singlet 202 and 006 peaks should be detected in this 2θ range. It was revealed that the crystal system of LaCrO_3 was rhombohedral at pressures of $5.4 \sim 10$ GPa. Although the doublet peak was observed at a pressure of 4.2 GPa, the coexistence of rhombohedral and orthorhombic phases was detected since the peak indexed as 006 of hexagonal description of the rhombohedral phase was observed. Diffraction peaks of LaCrO_3 at pressures of 0.8 and 3.1 GPa could be attributed to orthorhombic symmetry.

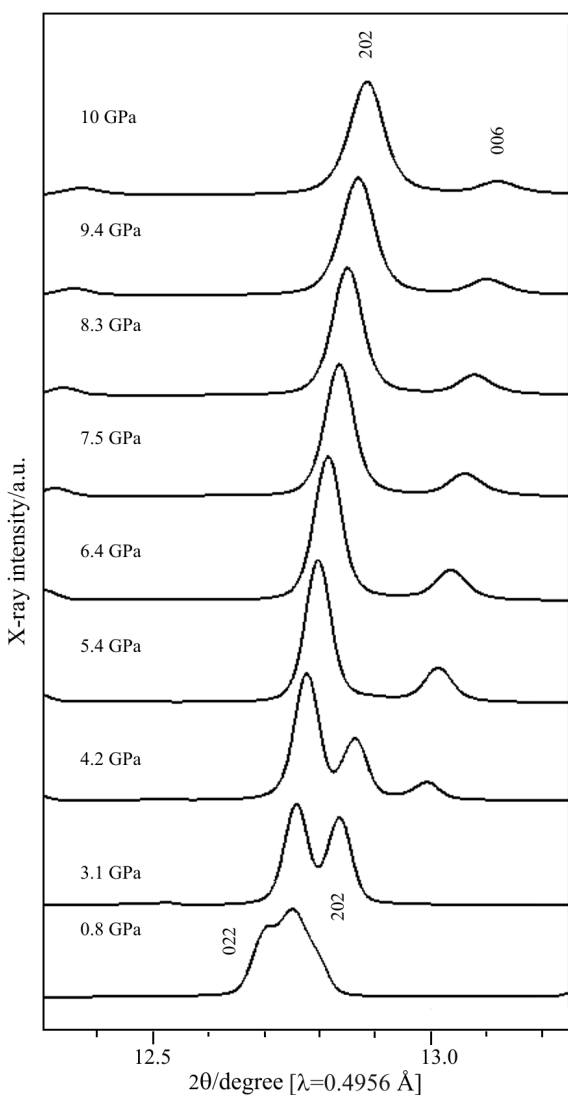


Fig. 5 X-ray diffraction peaks of LaCrO_3 at room temperature under various pressures. Peaks above 5.4 and below 3.1 GPa can be indexed to hexagonal and orthorhombic symmetries, respectively

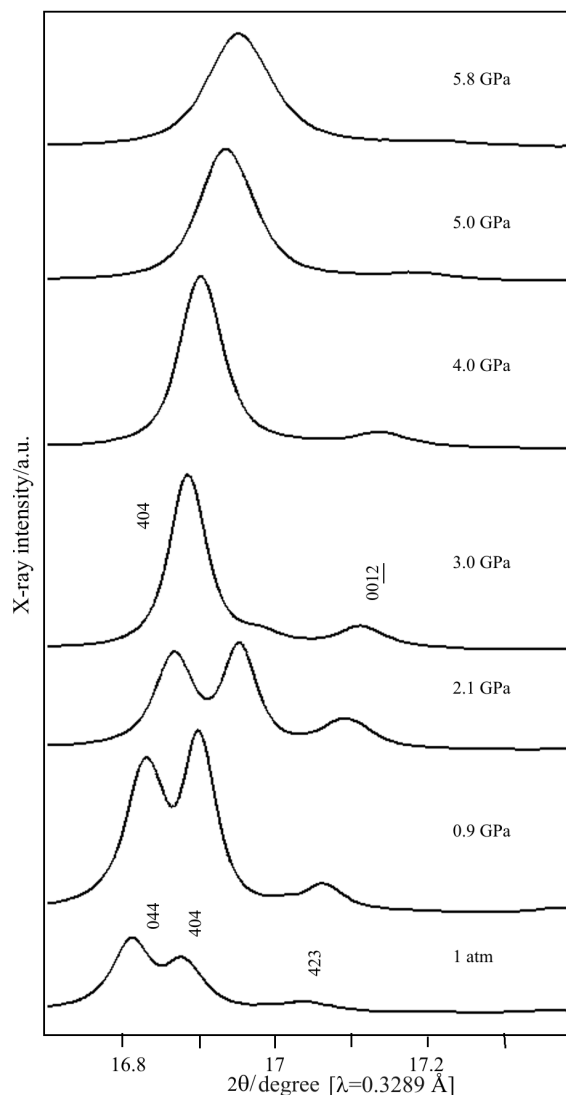


Fig. 6 X-ray diffraction peaks of LaGaO_3 at room temperature under various pressures. Peaks above 3.0 and below 2.1 GPa can be indexed to hexagonal and orthorhombic symmetries, respectively

Figure 6 shows the variation of X-ray diffraction peaks of LaGaO₃ with pressure. One doublet peak assigned to overlapping 044 and 404 reflections and a single 423 peak should be observed in the 2 θ range depicted in Fig. 6 for orthorhombic symmetry, while single 404 and 001 $\bar{2}$ peaks of hexagonal, i.e., rhombohedral symmetry should be detected using an X-ray source with a wavelength of 0.3289Å. It was concluded that crystal systems of LaGaO₃ are orthorhombic and rhombohedral below 2.1 and above 3.0 GPa, respectively, which is in agreement with the report by Kennedy *et al.* [10].

At room temperature, the phase transition pressures were 4.2~5.4 and 2.1~3.0 GPa for LaCrO₃ and LaGaO₃, respectively, which were higher than those predicted thermodynamically as discussed in the former section.

In addition, the observed phase transition pressure of LaCrO₃ was higher than that of LaGaO₃, despite the predicted phase transition pressure of LaCrO₃ being lower than that of LaGaO₃. The authors regard that these disagreements can be attributed to the slow kinetics of the phase transition at room temperature or to the assumption that ΔH and ΔV are independent of pressure.

Pressure dependence of lattice constants in rhombohedral LaCrO₃ and LaGaO₃

Figure 7 shows X-ray diffraction peaks of LaGaO₃ in the 2 θ range of 25.4~26.4° under various pressures. The wavelength of X-ray was 0.4970Å. In these measurements, pressure was increased from 4.1 to 9.4 GPa and then successively decreased to 4.2 GPa. Peak shift corresponding to the variation of lattice constants with pressure was observed and peaks were reversible with pressure in the rhombohedral phase. Lattice constants were calculated from the Bragg angle of the peaks.

Figure 8 shows the variation of lattice constants with pressure for rhombohedral LaCrO₃ and LaGaO₃ calculated from 220 and 208 peaks for the hexagonal description of the rhombohedral phase. The rhombohedral angle, denoted as α in Fig. 8, approaches 60° when the crystal symmetry approaches cubic, i.e., with higher crystal symmetry. In both LaCrO₃ and LaGaO₃, we observed a decrease of the rhombohedral axis, represented by a_r in Fig. 8, and an increase of α upon the application of pressure. The increase of deviation from α of 60° indicates that crystal symmetry becomes lower with increasing pressure at a constant temperature, following arrow (2) in Fig. 1. This behavior was compared with the variation of lattice constants with increasing temperature following arrow (1) in Fig. 1.

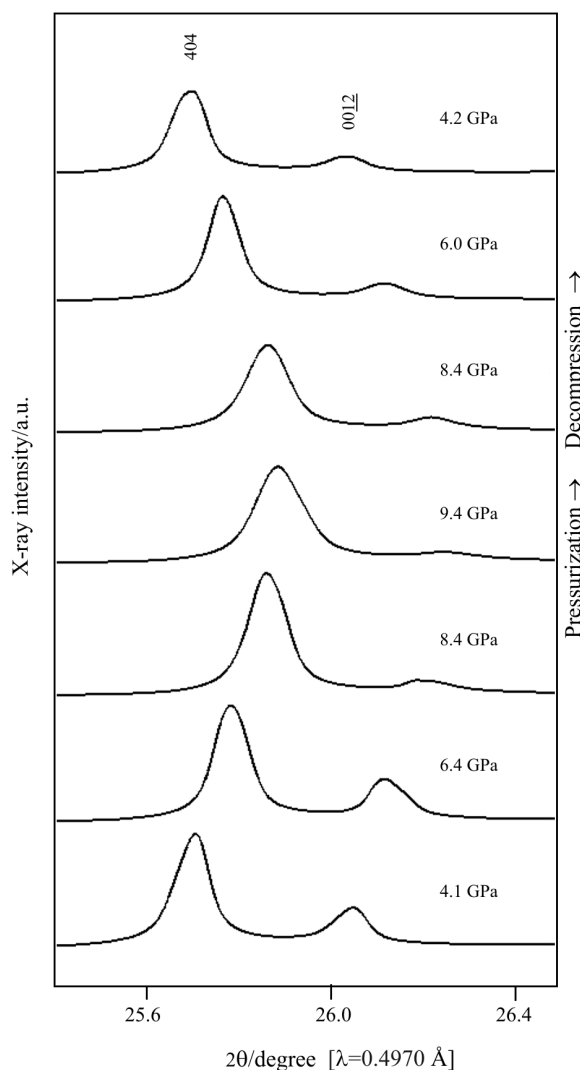


Fig. 7 X-ray diffraction peaks of LaGaO₃ at room temperature. The measurement was carried out with increasing pressure followed by a decrease of pressure

Figure 9 depicts the variation of lattice constants on temperature at 1 atm for rhombohedral LaCrO₃ and LaGaO₃ measured from high-temperature X-ray diffraction patterns [14, 17]. In addition to an almost linear thermal expansion in a_r of LaCrO₃ and LaGaO₃, a decrease of α to 60° with increasing temperature was observed. This indicates that crystal symmetry becomes higher following arrow (1) in Fig. 1. Berjoan and Coutures reported that the crystal structure of LaCrO₃ changed from rhombohedral to cubic at about 1650°C [18], showing qualitative agreement with the higher symmetry at elevated temperatures observed in this study. Thus, it was concluded that the application of pressure decreased the crystal symmetry, which was opposite to the increase with temperature for the same rhombohedral symmetry.

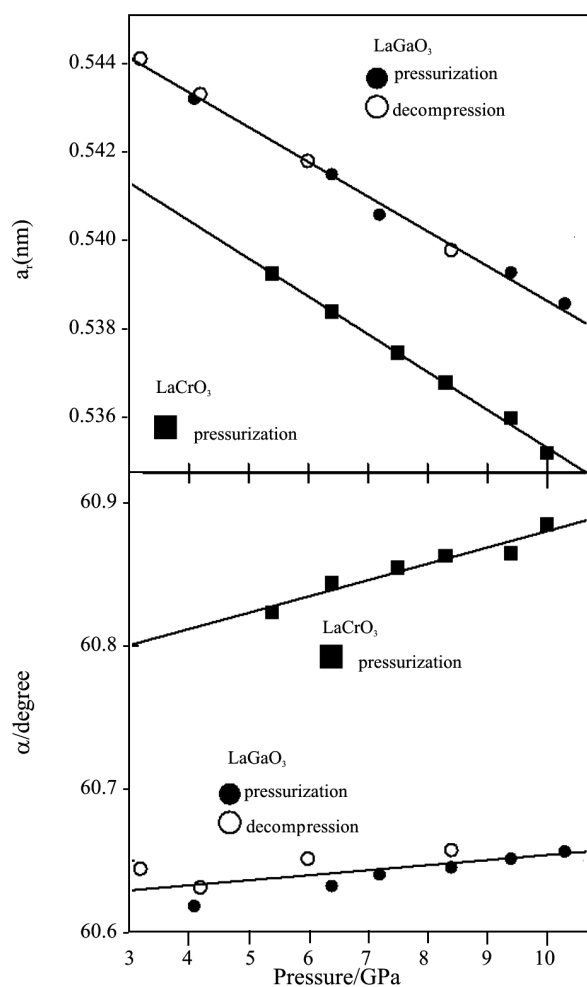


Fig. 8 Variation of rhombohedral lattice constants of LaCrO_3 and LaGaO_3 at room temperature with pressure. The symbols a_r and α denote the length and angle of the rhombohedral unit cell, respectively

From the data depicted in Fig. 9, the pressure dependence of the molar volumes of LaCrO_3 and LaGaO_3 was calculated and is depicted in Fig. 10. Since an almost linear decrease with increasing pressure was observed in both LaCrO_3 and LaGaO_3 , isothermal compressibility, κ which is defined as

$$\kappa = -1/V(dV/dP)_T,$$

can be calculated from the slope of Fig. 10. It was revealed that κ values of LaCrO_3 and LaGaO_3 were $4.4 \cdot 10^{-3} \text{ GPa}^{-1}$ and $4.1 \cdot 10^{-3} \text{ GPa}^{-1}$, respectively.

Conclusions

Structural phase transitions at room temperature upon the application of pressure in LaGaO_3 and LaCrO_3 , which were prospected from measurements of ΔH and ΔV at the phase transition under ambient pressure, were discovered by using high-pressure X-ray diffraction. It was revealed that the crystal structures of

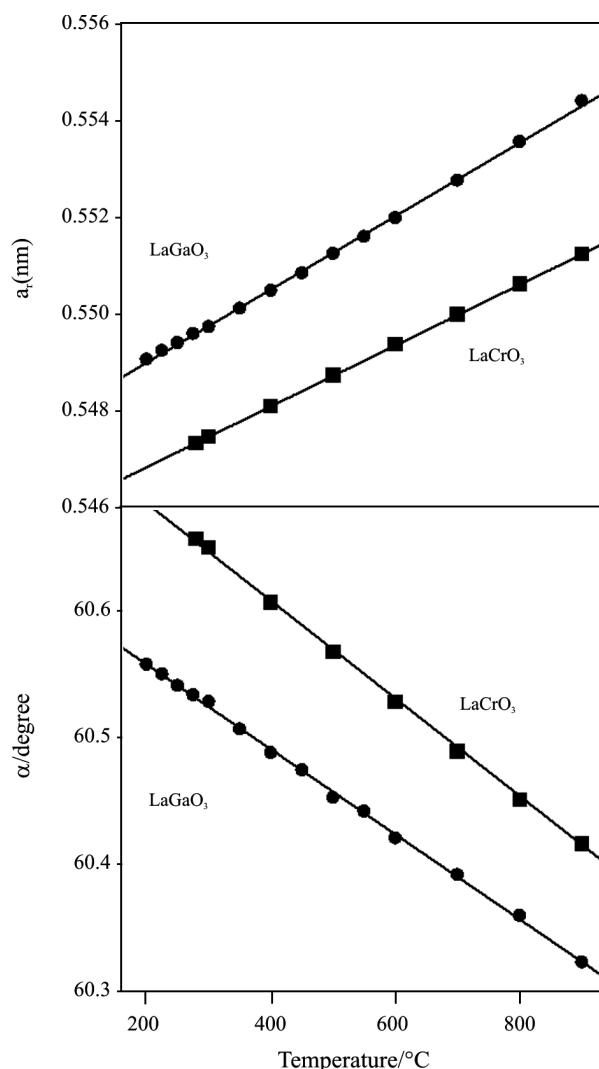


Fig. 9 Dependence of rhombohedral lattice constants of LaCrO_3 and LaGaO_3 at 1 atm on temperature. The symbols a_r and α denote the length and angle of the rhombohedral unit cell, respectively

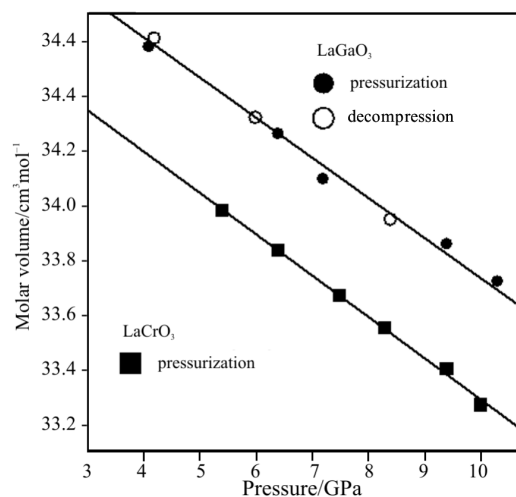


Fig. 10 Dependence of molar volume of LaCrO_3 and LaGaO_3 on pressure at room temperature

LaCrO₃ and LaGaO₃ changed completely from that of orthorhombic distorted perovskite to that of the rhombohedral distorted one upon the application of pressure of more than 5.4 and 3.0 GPa, respectively, at room temperature. Variations of lattice constants of the high-pressure rhombohedral phases of LaCrO₃ and LaGaO₃ with pressure indicated that crystal symmetry decreased with increasing pressure, whereas it increased with increasing temperature. The isothermal compressibilities were calculated to be $4.4 \cdot 10^{-3}$ GPa⁻¹ and $4.1 \cdot 10^{-3}$ GPa⁻¹ for LaCrO₃ and LaGaO₃, respectively.

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