

## Original Paper

# Thermal Expansion of the CZ-Grown LaAlO<sub>3</sub> Single Crystal at High Temperatures

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The structural evolution of lanthanum aluminum trioxide (LaAlO<sub>3</sub>) crystals grown by the Czochralski (CZ) method has been investigated by the *in-situ* single-crystal X-ray diffraction method in the temperature range between 296 and 1195 K. The square of the AlO<sub>6</sub> octahedral rotation angle in the rhombohedral structure decreased linearly near the transition temperature, suggesting that a second-order phase transition occurs at *circa* 839 K. Changes in the volumetric thermal expansion coefficient show a significant discontinuity at the transition point, supporting an experimental evidence by dilatometry in literature.

Key Words: Lanthanum Aluminum Oxide, Single Crystal, Czochralski, Thermal Expansion, Phase Transition, High Temperature

## 1. Introduction

Crystals of lanthanum aluminum trioxide (LaAlO<sub>3</sub>) are used for the low-loss microwave and dielectric resonance applications in polycrystalline forms[1,2]. Single-crystals are also used as substrates for the epitaxial growth of various high- $T_c$  superconductors, magnetic and ferroelectric thin films because of its good lattice match to perovskite-related crystals. Recently, the atomic layer epitaxy of LaAlO<sub>3</sub> on SrTiO<sub>3</sub>, or *vice versa*, has drawn considerable attention since a two-dimensional superconducting behavior was observed at the interface[3]. Deposition temperatures by molecular beam epitaxy or pulsed laser deposition lie near the ferroelectric phase transition temperature ( $T_c$ ) of LaAlO<sub>3</sub>, *ca.* 800 K[4], at which the crystal transforms from cubic to rhombohedral. Therefore, the thermal expansion behavior around  $T_c$  presumably plays an important role in the quality of fabricated interface.

A significant discontinuity in the linear thermal expansion coefficient of LaAlO<sub>3</sub> at  $T_c$  was reported for the sintered polycrystalline material by the dilatometry study[5]. The thermal expansion behavior of the unit cell dimensions was elucidated using cubic polynomial functions by the high-temperature powder neutron diffraction studies[6,7]. The volumetric expansion coefficients calculated from the neutron data[7], however, shows no significant discontinuity at  $T_c$ . No single-crystal study on the thermal expansion on LaAlO<sub>3</sub> is available as far as the authors are aware. The present study was thus undertaken to provide information on the thermal expansion properties of the commercially available single-crystal grown by the Czochralski (CZ) method.

## 2. Experimental

Crystal fragments were taken from the polished wafer of the CZ grown crystal (Shinkosha, Co., Ltd). The surface of the crystal was in the [100] orientation with respect to the pseudo-cubic unit cell. A preliminary check about the extinction rules of reflections of the rhombohedral LaAlO<sub>3</sub> at the room temperature was carried out at the beamline 14A, KEK, using a four-circle diffractometer[8]. *In-situ* X-ray diffraction experiments were carried out at elevated temperatures using a single-crystal CCD diffractometer (Smart Apex II, Bruker) with MoK $\alpha$  laboratory source[9]. Two crystals are ground into spheres of 80  $\mu$ m in diameter and mounted on a silica glass capillary by Sauereisen cement (#970000, Niraco Co.).

The samples (wj12 and wj18) were soaked in the preheated nitrogen gas stream. The temperature at the crystal position was calibrated by the K-type fine gauge thermocouple (KFC-50-200-100, Anbe SMT Co.).

Intensity distribution in reciprocal space was investigated through the sets of contiguous frame data so that more than 99 % of all the possible reflections within  $2\theta < 60^\circ$  can be measured. Each of the frame data was taken by either  $\omega$  or  $\phi$  scan techniques in the range of  $0.3^\circ$  with an exposure time of 5 s. It took 2 h to collect a set of data at one temperature. The experimental temperatures span from 296 to 1195 K inclusive, as listed in Table 1 in time order. Integrated intensities were extracted from the frame data. The cell parameters were refined from all the observed reflections in the integration process. The spherical absorption correction was applied to the intensity data. The SHELXL program[10] in the WinGX program package[11] was used for the structure refinement.

The space group of the rhombohedral LaAlO<sub>3</sub> has historically long been assumed as  $R\bar{3}c$ [6,7,12]. Although recent Raman spectroscopic study on pure LaAlO<sub>3</sub>[13] and X-ray studies on Sr and Ti double-doped LaAlO<sub>3</sub>[14] suggested a possible occurrence of  $R3c$  or  $R\bar{3}$  instead of  $R\bar{3}c$ , the present study followed the assumption of  $R\bar{3}c$ . This is firstly because the present study concerns the determination of phase transition temperature and the behavior of the thermal expansion of LaAlO<sub>3</sub> rather than the structure itself, and secondly because the aforementioned high-speed data collection scheme is essentially opposed to the precise analysis to detect a subtle deviation from the ideal  $R\bar{3}c$  structure in rhombohedral modification. The space group  $Pm\bar{3}m$  was assumed for the cubic phase[6,7]. The final structure parameters are also given in Table 1.

## 3. Results and Discussion

The rhombohedral-cubic phase transition can be seen most clearly in the changes of interatomic distance around La atoms with temperature, as shown in Fig.1. The La atoms in the rhombohedral structure is surrounded by twelve O atoms at three different distances; three O at the shortest, three O at the longest, and the remaining six O in the middle. With increasing temperature, the differences among these La-O distances become smaller and finally disappear in the cubic structure. The difference between the longest and shortest La-O distances becomes larger in the cooling process

Table. 1 Crystal data and structure parameters for LaAlO<sub>3</sub> at various temperatures in experimental time order.

| Sample | Process    | Space Group | Temp. (K) | R1 <sup>*1</sup> /refs <sup>*2</sup> | a (Å)     | c (Å)      | x <sub>O</sub> <sup>*3</sup> | U <sub>La</sub> (Å <sup>2</sup> ) | U <sub>Al</sub> (Å <sup>2</sup> ) | U <sub>O</sub> (Å <sup>2</sup> ) |
|--------|------------|-------------|-----------|--------------------------------------|-----------|------------|------------------------------|-----------------------------------|-----------------------------------|----------------------------------|
| wj12   | On heating | R-3c        | 296       | 3.36/114                             | 5.3572(3) | 13.1183(9) | 0.5174(9)                    | 0.0054(2)                         | 0.0045(9)                         | 0.011(1)                         |
|        | On heating | R-3c        | 590       | 3.23/102                             | 5.3704(2) | 13.1523(8) | 0.5146(7)                    | 0.0090(2)                         | 0.0072(9)                         | 0.014(1)                         |
|        | On heating | R-3c        | 670       | 2.40/95                              | 5.3763(3) | 13.1618(9) | 0.5120(5)                    | 0.0105(2)                         | 0.0088(7)                         | 0.0157(9)                        |
|        | On heating | R-3c        | 738       | 1.57/79                              | 5.3793(2) | 13.1728(8) | 0.5093(3)                    | 0.0104(1)                         | 0.0083(5)                         | 0.0162(7)                        |
|        | On heating | R-3c        | 787       | 2.06/93                              | 5.3830(3) | 13.1805(9) | 0.5071(3)                    | 0.0109(1)                         | 0.0087(6)                         | 0.0169(9)                        |
|        | On heating | R-3c        | 836       | 2.87/79                              | 5.3858(3) | 13.1863(9) | 0.5024(2)                    | 0.0115(2)                         | 0.009(1)                          | 0.017(1)                         |
|        | On heating | Pm-3m       | 885       | 1.17/31                              | 3.8097(2) |            |                              | 0.0121(1)                         | 0.0098(4)                         | 0.0180(6)                        |
| wj12   | On cooling | Pm-3m       | 856       | 1.20/31                              | 3.8093(2) |            |                              | 0.01123(8)                        | 0.0089(4)                         | 0.0167(6)                        |
|        | On cooling | R-3c        | 836       | 2.18/73                              | 5.3862(2) | 13.1917(6) | 0.50307(23)                  | 0.0118(1)                         | 0.0098(6)                         | 0.0179(8)                        |
|        | On cooling | R-3c        | 816       | 3.3/74                               | 5.3848(2) | 13.1880(6) | 0.50438(16)                  | 0.0106(1)                         | 0.0091(4)                         | 0.0170(0)                        |
|        | On cooling | R-3c        | 787       | 3.8/83                               | 5.3826(2) | 13.1834(6) | 0.50663(30)                  | 0.0114(1)                         | 0.0080(5)                         | 0.016(9)                         |
|        | On cooling | R-3c        | 758       | 2.6/83                               | 5.3812(2) | 13.1795(5) | 0.50877(34)                  | 0.0104(1)                         | 0.0078(4)                         | 0.0163(7)                        |
|        | On cooling | R-3c        | 738       | 2.9/88                               | 5.3800(2) | 13.1764(6) | 0.50928(35)                  | 0.0103(1)                         | 0.0075(4)                         | 0.0161(7)                        |
|        | On cooling | R-3c        | 670       | 3.1/123                              | 5.3763(2) | 13.1663(6) | 0.51278(30)                  | 0.0085(3)                         | 0.0074(13)                        | 0.018(10)                        |
| wj18   | On cooling | R-3c        | 296       | 3.3/343                              | 5.3603(1) | 13.1267(3) | 0.51932(42)                  | 0.00511(3)                        | 0.0046(2)                         | 0.0097(3)                        |
|        | On heating | Pm-3m       | 846       | 1.61/32                              | 3.8080(2) |            |                              | 0.0114(2)                         | 0.0098(9)                         | 0.016(1)                         |
|        | On heating | Pm-3m       | 866       | 1.61/32                              | 3.8089(2) |            |                              | 0.0122(2)                         | 0.0105(8)                         | 0.018(1)                         |
|        | On heating | Pm-3m       | 885       | 1.73/32                              | 3.8100(2) |            |                              | 0.0096(6)                         | 0.022(4)                          | 0.012(3)                         |
|        | On heating | Pm-3m       | 934       | 1.68/32                              | 3.8119(2) |            |                              | 0.0114(5)                         | 0.018(3)                          | 0.014(3)                         |
|        | On heating | Pm-3m       | 984       | 1.42/32                              | 3.8159(2) |            |                              | 0.0135(2)                         | 0.010(1)                          | 0.018(1)                         |
|        | On heating | Pm-3m       | 1195      | 1.19/43                              | 3.8259(2) |            |                              | 0.0149(2)                         | 0.0130(8)                         | 0.024(1)                         |

\*1;  $R1 = \sum ||F_o| - |F_c|| / \sum |F_o|$  \*2; Number of independent reflections used for refinement. \*3; Fractional parameter x of O atom.

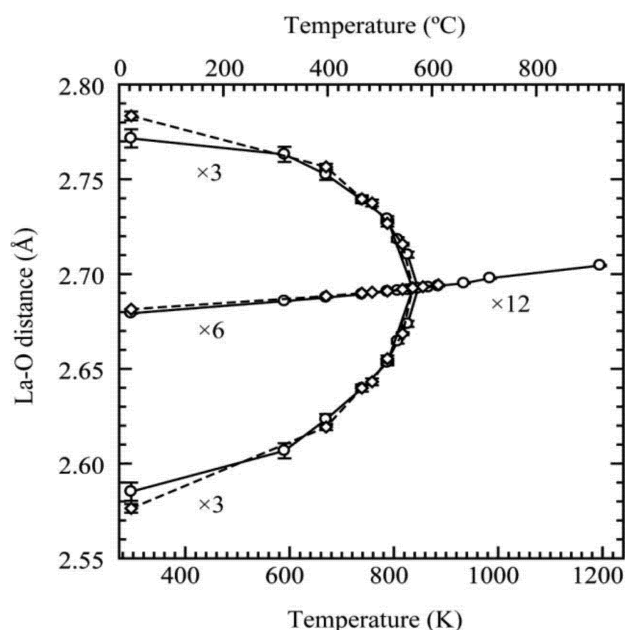


Fig.1 Temperature dependence of La-O interatomic distances in LaAlO<sub>3</sub>. Data points on heating (○) are connected by solid lines and those on cooling (◇) are done by dashed ones as guides for the eye.

compared with the heating, suggesting that the heat treatment in the present diffraction experiment has released the internal strain in the as-grown crystal to some extent.

In the rhombohedral structure, the AlO<sub>6</sub> octahedra are slightly rotated about the [111] axis of the pseudo-cubic unit cell. The rotation angle  $\varphi$  is related to the fractional coordinate  $x_O$  of the O atom as;

$$\tan \varphi = 2\sqrt{3}(x_O - 0.5). \quad (1)$$

If the phase transition is of the second-order,  $\varphi^2$  decreases linearly toward the phase transition temperature  $T_c$  in the

rhombohedral structure[15]. As shown in Fig.2, the linearity on heating was well represented in the temperature range between 590 K and 826 K as;

$$\varphi^2 = 8.561 \times 10^{-3} - 1.020 \times 10^{-5} T. \quad (2)$$

The phase transition temperature  $T_c$  was estimated to be 839 K by extrapolating the equation (2) at  $\varphi = 0$ . The neutron powder data[7] were also plotted in Fig.2, resulting in  $T_c = 841$  K in accordance with the present data. The octahedral rotation angles in the present crystal are generally small compared with the neutron

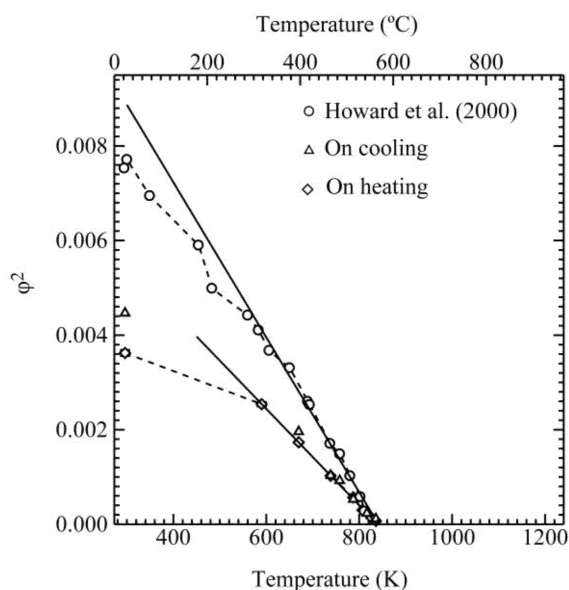


Fig.2 Temperature dependence of the squared rotation angle (in radian) of AlO<sub>6</sub> octahedron in rhombohedral LaAlO<sub>3</sub> near the phase transition temperature. The solid and straight line of the present study corresponds to the equation (2). Dashed lines connect data points of the present study on heating and those in literature[7], just as guides for the eye.

powder diffraction data. Since  $\phi^2$  on cooling become slightly larger than those on heating, the release of internal strain has been accomplished partially by the heat treatment.

The unit cell parameters ( $a_H$  and  $c_H$  in Å) of the rhombohedral structure in the hexagonal setting were approximated by the quadratic functions of temperature  $T$  (K);

$$a_H = 5.34557 + 3.40221 \times 10^{-5} T + 1.62311 \times 10^{-8} T^2 \quad (3)$$

$$c_H = 13.0930 + 7.04397 \times 10^{-5} T + 5.01839 \times 10^{-8} T^2. \quad (4)$$

The unit cell parameter ( $a_C$  in Å) of the cubic structure was best approximated by the linear function of temperature;

$$a_C = 3.76407 + 5.18667 \times 10^{-5} T. \quad (5)$$

The higher order terms were negligible in the cubic structure compared with the rhombohedral one. The reduced pseudo-cubic cell volumes of the rhombohedral and cubic structures,  $V_R$  and  $V_C$  (Å<sup>3</sup>), respectively, are shown in Fig.3. Their changes against temperature were approximated by the quadratic and linear functions, respectively;

$$V_R = V_{\text{hex}} / 6 = 54.0347 + 8.1857 \times 10^{-4} T + 7.02994 \times 10^{-7} T^2, \quad (6)$$

$$V_C = 53.3618 + 2.2100 \times 10^{-3} T. \quad (7)$$

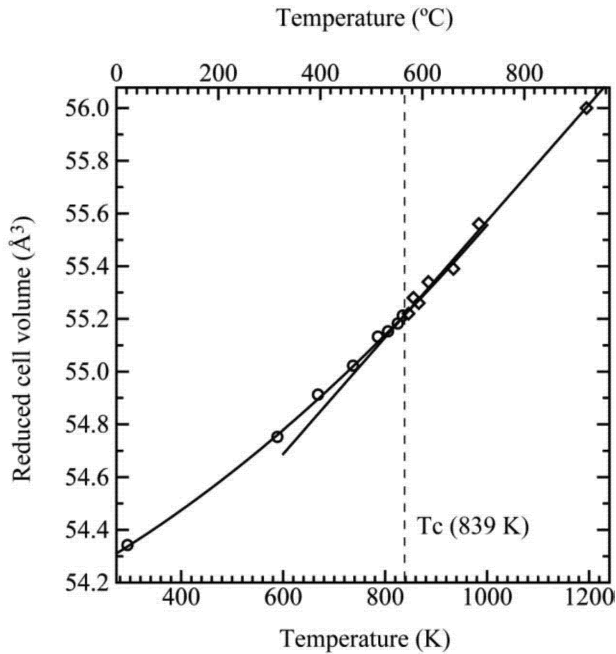


Fig.3 Temperature dependence of the pseudo-cubic cell volume of rhombohedral (o) and cubic (□) structures of LaAlO<sub>3</sub>. Solid lines in rhombohedral and cubic structures correspond to equations (6) and (7), respectively.

The higher order terms were again negligibly small in the cubic structure compared with the rhombohedral one. The volumetric thermal expansion coefficients  $\alpha_V$  (K<sup>-1</sup>) are calculated from;

$$\alpha_V = (\partial V_T / \partial T) / V_{T_0}, \quad (8)$$

where  $V_T$  and  $V_{T_0}$  are the reduced cell volumes at  $T$  and  $T_0$ , respectively. In this paper we used  $T_0 = 300$  K and  $V_{T_0} = 54.344$  Å<sup>3</sup>. Values of  $(\partial V_T / \partial T)$  were obtained by differentiating the equations (6) and (7) to avoid scattering when the measured data were used. Changes in  $\alpha_V$  with temperature are plotted in Fig.4, as well as those obtained from the dilatometry study[5], and computational study[16], and the neutron powder diffraction data[7]. The linear thermal expansion coefficient reported on the sintered LaAlO<sub>3</sub> rod by dilatometry[5] was multiplied by 3 for conversion. The  $\alpha_V$  for neutron data were obtained by differentiating the cubic polynomial expressions given in the paper[7]. A significant discontinuity in  $\alpha_V$  at  $T_c$  can be seen in the dilatometry data in Fig.4. The present single-crystal study also confirms the discontinuity at  $T_c$ , though

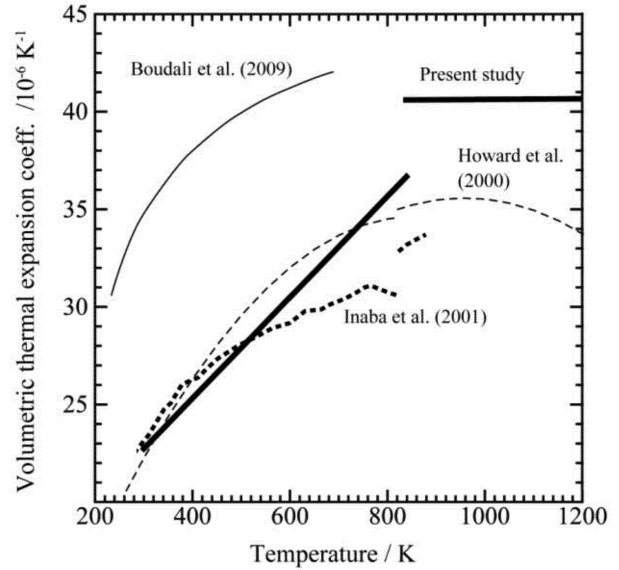


Fig.4 Temperature dependence of volumetric thermal expansion coefficient of LaAlO<sub>3</sub> (thick-solid line) compared with dilatometric experimental study (thick-dashed line)[5], powder neutron diffraction study (thin-dashed line)[7], and computational study (thin-solid line)[16].

the  $\alpha_V$  values are slightly larger at high temperatures compared with the dilatometry study. On the other hand, the discontinuity is less obvious in the neutron diffraction data.

Volume expansion coefficient  $\alpha_V$  can be expressed as

$$\alpha_V = \gamma C_V / B_T V, \quad (9)$$

using specific heat capacity at constant volume ( $C_V$ ), isothermal bulk modulus ( $B_T$ ), molar volume ( $V$ ) and the Grüneisen parameter ( $\gamma$ )[17]. Among them, only  $C_V$  increases drastically as a function of temperature and approaches to a constant value of  $\sim 25$  J mol<sup>-1</sup> K<sup>-1</sup> at high temperatures according to the law of Dulong and Petit[18]. Since the other parameters change modestly with temperature,  $\alpha_V$  also has a temperature dependency similar to  $C_V$ . Actually, this is exemplified in the result of the first-principle calculation on LaAlO<sub>3</sub>[16], which is also depicted in Fig.4. Our differentiation of the cubic cell volume of the neutron data expressed in cubic polynomial[7] resulted in a decaying curve at higher temperatures. This may suggest a potential problem in approximation using high orders in polynomial expression for limited observations both in number and accuracy.

#### 4. Summary

The thermal expansion behavior and the ferroelectric phase transition temperature of the CZ-grown LaAlO<sub>3</sub> crystal have been elucidated by the *in-situ* single-crystal X-ray diffraction technique at elevated temperatures. The present study confirms qualitatively the discontinuity in the volumetric thermal expansion coefficient at  $T_c$  observed by the dilatometry study in literature. Given the relatively large discontinuity in the volumetric thermal expansion coefficient of LaAlO<sub>3</sub> at  $T_c$ , the deposition of the substance by atomic layer epitaxy is recommended to be carried out below  $T_c$  which has been estimated at 839 K.

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