

# Measurement of thermal expansion coefficient of $\text{LaCrO}_3$

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## Abstract

Thermal expansion coefficients of  $\text{LaCrO}_3$  and  $\text{Al}_2\text{O}_3$  were measured using a push-rod type dilatometer in the temperature range from 100 to 873 K. The error of the measurement depending on the position of the thermocouple in the dilatometer was also investigated. The thermal expansion coefficient of  $\text{Al}_2\text{O}_3$  in the temperature range from 100 to 873 K generally agreed with the literature value. Anomalies in the thermal expansion coefficient were observed clearly at 283 and 528.5 K in  $\text{LaCrO}_3$ . The first anomaly is a volume expansion due to the transition from an anti-ferromagnetic to a paramagnetic state, the second one is a volume shrinkage due to the transition from an orthorhombic to a rhombohedral structure. The thermal expansion coefficient measured using the thermocouple on the reference side was about 1% higher than that using the thermocouple attached on the sample. The error of the transition temperature due to the position of the thermocouple was also investigated. © 2000 Elsevier Science B.V. All rights reserved.

*Keywords:* Thermal expansion coefficient; Push-rod type dilatometer; Alumina; Lanthanum chromite; Phase transition temperature

## 1. Introduction

Thermal expansion coefficient is a second derivative of Gibbs energy and is one of the most important thermodynamic properties of materials. Even a small anomaly in the thermal expansion coefficient, for example, shows a phase transition like that in the heat capacity. Therefore, the accurate measurement of the thermal expansion coefficient, not the thermal expansion, is very important, since the thermal expansion versus temperature is not sensitive enough to detect a small anomaly due to phase transition.

The method of the push-rod type dilatometer for measuring thermal expansion is experimentally simple, reliable, and easy to automate [1]. The thermal expansion coefficients  $\alpha$  at a temperature  $T$  in the push-rod type dilatometer can be written as

$$\alpha = \frac{dL/dT}{L} \quad (1)$$

$$dL = dL_d + dL_r, \quad (2)$$

where  $L$  is the length of a sample at room temperature,  $dL$  and  $dL_r$  the small changes in the length of the sample and the reference, respectively, accompanied by a very small increase of the temperature  $dT$  and  $dL_d$  is the differential change in the length between the sample and the reference, which is the signal of the push-rod type dilatometer.

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The errors due to measurement of the thermal expansion coefficient can be described as

$$\frac{\delta\alpha}{\alpha} = \frac{\delta L}{L} + \frac{\delta(dL)}{dL} + \frac{\delta(dT)}{dT} \quad (3)$$

$$\frac{\delta(dL)}{dL} = \frac{\delta(dL_d)}{dL_d} + \frac{\delta(dL_r)}{dL_r},$$

where  $\delta$  means the error of each variable. The first and second terms in Eq. (3) represent the error to measure the sample length and the increment of the sample length. The third term consists of the error due to the temperature difference between sample and temperature sensor and temperature distribution in the sample. The error to measure the sample length is very small and the increment of the reference length  $dL_r$  using fused silica compared with that of the sample is usually one order of magnitude smaller than that of the sample and can be neglected by using the proper reference value. Therefore, Eq. (3) can be approximately reduced to

$$\frac{\delta\alpha}{\alpha} = \frac{\delta(dL_d)}{dL_d} + \frac{\delta(dT)}{dT} \quad (4)$$

The second term in Eq. (3) or the first term in Eq. (4) is determined by the type of dilatometer and the second term in Eq. (4) is the common source of error in various types of dilatometer [2]. The temperature derivative of thermal expansion, namely, the instantaneous thermal expansion coefficient has not been given in most cases using the push-rod type dilatometer, but the averaged thermal expansion coefficient over a wide temperature range has been reported. One of the most important problems to derive the thermal expansion coefficient using the push-rod type dilatometer is the error of the temperature measurement, since the temperature sensor is not usually attached to the sample and the measurement is usually performed at a constant heating rate.

Lanthanum chromite ( $\text{LaCrO}_3$ ) is a perovskite-type oxide with very refractory properties with melting point higher than 2673 K and high chemical stability over wide temperatures and oxygen partial pressures. Doped lanthanum chromite is the most commonly used as an interconnect of solid-oxide fuel cells (SOFCs) [3]. The doping of lanthanum chromite with a lower valence ion influences the properties of the material in many ways; adjustment of thermal

expansion [4–6], elimination of phase transition [4–6] and increase of electrical conductivity [3,6].

$\text{LaCrO}_3$  is reported to have the two phase transitions around 300 and 530 K. The former transition is ascribed to magnetic transition from an anti-ferromagnetic to a paramagnetic state by means of adiabatic calorimetry [7], neutron diffraction [8], static magnetic susceptibility [9,10] and electron paramagnetic resonance [11]. This transition has not been reported by the measurement of the thermal expansion coefficient. The latter transition is a structural one from orthorhombic to rhombohedral [12,13] accompanied by a large volume shrinkage [5,6,14,15] and an endothermic effect [7,15–17].

There are many reports about the thermal expansion coefficient of  $\text{LaCrO}_3$  above room temperature region [3,5,6,14,18–21]. It is, however, noted that most of the thermal expansion coefficients reported were average thermal expansion coefficients over wide temperature ranges, which do not give a practical meaning especially when phase transitions exist. The temperature dependence of the thermal expansion coefficient for  $\text{LaCrO}_3$  has scarcely been reported except for that by Tolochko et al. [14] in the range from 350 to 730 K. The thermal expansion coefficient of  $\text{LaCrO}_3$  below room temperature has not been reported.

In the present paper, the thermal expansion coefficients of  $\text{LaCrO}_3$  and  $\text{Al}_2\text{O}_3$  were measured in the temperature range from 100 to 873 K. The error of the measurement depending on the position of the thermocouple in the dilatometer was also investigated.

## 2. Experimental

The apparatus used was a push-rod type differential dilatometer (Rigaku TMA8310) which is schematically shown in Fig. 1. The difference of the thermal expansions between the sample and the reference rod was detected by the differential transformer through push-rods of fused silica. The thermal expansion of the sample was given by subtracting the thermal expansion of the reference rod using reference data [22]. The temperature detected by using the thermocouple inserted into the center hole of the reference rod (at the position B in Fig. 1) is often regarded as the temperature of the sample in the differential type of dilatometer, because drilling a hole in the sample for

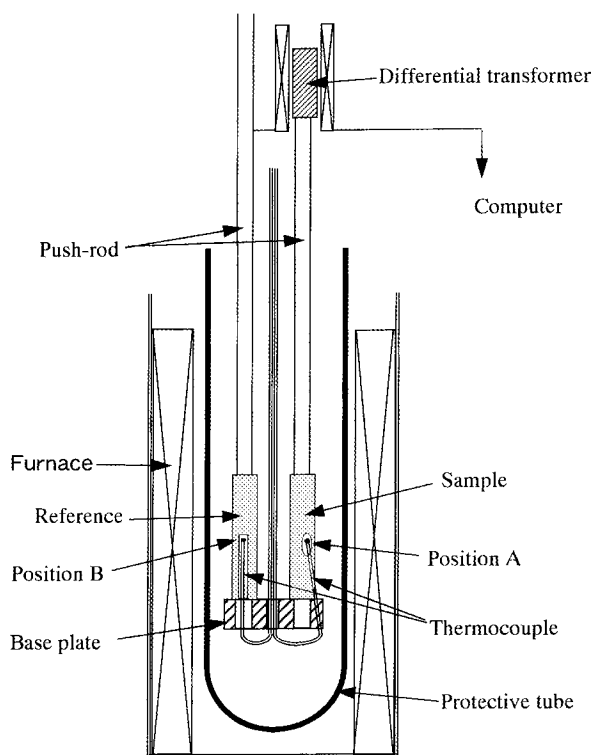


Fig. 1. Schematic drawing of the differential dilatometer.

setting the thermocouple or bonding the thermocouple on the sample is practically difficult. In the present study, the temperature of the sample was measured at the position A in Fig. 1, where the thermocouple was bonded to the sample by a ceramic bonding agent. The temperature was also measured at the position B in Fig. 1 (reference side), which has usually been regarded as the apparent temperature of the sample to obtain the thermal expansion coefficient. The used thermocouples were the platinel-type and were calibrated with the melting temperatures of In with 99.9% purity and Pb with 99.99% purity. The reference sample used was a fused silica rod of 5 mm in diameter and 20 mm in length. The temperature differences between the sample (position A) and the reference (position B) were measured. The sample and the reference were pushed through fused silica rods using the weight of 40 g. The sample and the reference sample were surrounded by the cylindrical furnace as shown in Fig. 1. The measurement of the thermal expansion was performed in the temperature range from 100 to 873 K at the heating rates of 2, 5 and

10 K min<sup>-1</sup>. The cooling of the apparatus to 100 K was done by using liquid N<sub>2</sub> poured into a dewar flask attached outside of the furnace. The heating rate was controlled using a thermocouple attached in the furnace. The data acquisition of the differential length and the temperature was conducted at every 0.5, 0.2 and 0.1 s at the heating rates of 2, 5 and 10 K min<sup>-1</sup>, respectively, whose times correspond to 0.017 K for all the heating rates.

Since the data of the length and the temperature are both functions of time, Eq. (1) is expressed by

$$\alpha = \left[ \frac{(\delta L / \delta t) / (\delta T / \delta t)}{L} \right], \quad (5)$$

where  $\delta t$  is a time interval of sampling. A derivative of thermal expansion with respect to time at each sampling point:  $\delta L / \delta t$  was calculated after smoothing using a 100-point moving average of 46,000 data. Then, 1000 data of  $\delta L / \delta t$  and  $\delta T / \delta t$  were extracted and stored as ASCII codes. Since the heating rate was controlled using the thermocouple at the furnace, the heating rate at the sample,  $\delta T / \delta t$ , did not become constant as described later. The thermal expansion coefficient was then obtained using these data and Eq. (5) and subsequent nine-point moving average.

Samples of LaCrO<sub>3</sub> for the measurement of the thermal expansion coefficient were provided by Central Research Institute of Electric Power Industry, Japan. The preparation of sintered LaCrO<sub>3</sub> was the ordinary ceramic powder method as described in [6]. The structure of the sintered LaCrO<sub>3</sub> was confirmed to be a single phase of the orthorhombic structure by X-ray diffraction analysis. The sample was a rectangular shape of about 3.5 × 3.2 × 20 mm<sup>3</sup>. An alumina sample sintered using 99.9% purity powder was also used for the measurement of the thermal expansion coefficient. It was a cylindrical rod of 5 mm in diameter and 20 mm in length.

### 3. Results and discussion

#### 3.1. Measurement of thermal expansions coefficient of Al<sub>2</sub>O<sub>3</sub>

The measured thermal expansion coefficient of Al<sub>2</sub>O<sub>3</sub> is shown as a function of temperature in Fig. 2, where the thermal expansion coefficient

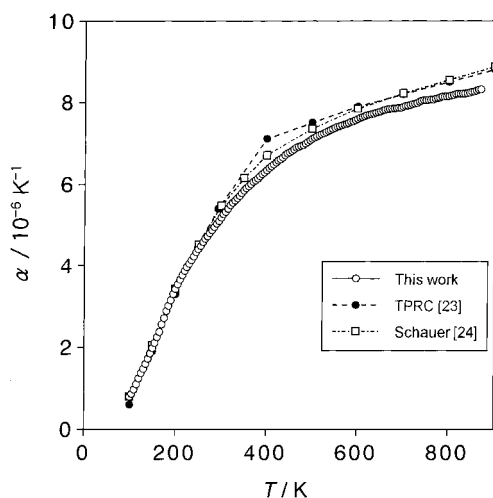


Fig. 2. Thermal expansion coefficient  $\alpha$  of  $\text{Al}_2\text{O}_3$ .

reported for polycrystalline alumina by TPRC [23] and that by Schauer [24] are also shown for comparison. The latter [24] is very close to that recommended by CODATA [25]. Those values of the present study and the literature [24] are given in Table 1. The thermal expansion coefficient of the present study below 300 K agrees satisfactorily with that reported by Schauer [24] and that reported by TPRC [23], but is

Table 1  
Linear thermal expansion coefficient of  $\text{Al}_2\text{O}_3$

$T$ (K)	$\alpha^a$ ( $10^{-6} \text{ K}^{-1}$ )	$\alpha^b$ ( $10^{-6} \text{ K}^{-1}$ )
100	0.79	0.8
150	1.98	2.05
200	3.42	3.43
250	4.41	4.52
300	5.18	5.47
350	5.85	6.15
400	6.33	6.7
450	6.77	–
500	7.10	7.35
550	7.37	–
600	7.59	7.85
650	7.77	–
700	7.89	8.22
750	8.06	–
800	8.16	8.55
850	8.26	–

<sup>a</sup> Data of the present study from 'this work'.

<sup>b</sup> Data from [24].

slightly smaller above 500 K. The larger value at 400 K reported by TPRC [23] may be due to the fact that the thermal expansion coefficient at 400 K is near the edge of the two polynomial equations in the temperature regions below and above 293 K, which were obtained from the various sources of reference data.

### 3.2. Thermal expansion coefficient of $\text{LaCrO}_3$

Fig. 3 shows the thermal expansion of  $\text{LaCrO}_3$  at the heating rate of  $5 \text{ K min}^{-1}$ . An obvious anomaly of the thermal expansion is observed around 530 K and a slight change in the thermal expansion curve is seen around 300 K in Fig. 3. The anomaly around 530 K is due to the structural transition from an orthorhombic to a rhombohedral phase [12,13] as reported to be from 513 to 554 K by thermal expansion measurement [5,6,14,19]. The slight change in the thermal expansion curve around 300 K is probably due to the magnetic transition from an anti-ferromagnetic to a paramagnetic state [7–9,11]. This magnetic transition, however, has not been reported by the thermal expansion measurement, since it is very slight change in the thermal expansion. Gildu et al. [26] measured the volume expansion using low-temperature X-ray diffraction between 123 and 420 K every 20 K, but they did not report the anomaly around 300 K. The thermal expansion coefficients of  $\text{LaCrO}_3$  as a function of

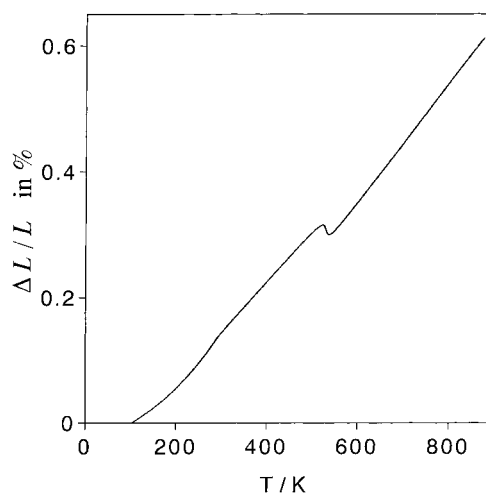


Fig. 3. Thermal expansion of  $\text{LaCrO}_3$  at a heating rate of  $5 \text{ K min}^{-1}$ .

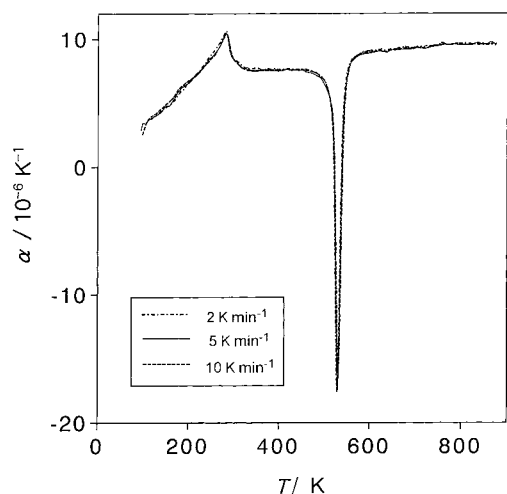


Fig. 4. Thermal expansion coefficient of  $\text{LaCrO}_3$  at heating rates of 2, 5 and  $10 \text{ K min}^{-1}$ .

temperature at the heating rate of 2, 5 and  $10 \text{ K min}^{-1}$  are shown in Fig. 4. The magnified figure of the anomalous region around 530 K in Fig. 4 is Fig. 5. The thermal expansion coefficients at the heating rate of 2, 5 and  $10 \text{ K min}^{-1}$  are almost the same regardless the heating rate except for the temperature region of the phase transition as seen in Fig. 4. The smoothed values of the thermal expansion coefficient of  $\text{LaCrO}_3$  at the heating rate of  $2 \text{ K min}^{-1}$  are listed in Table 2

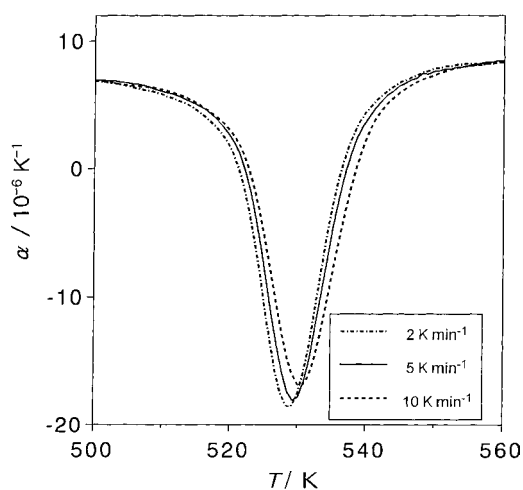


Fig. 5. Thermal expansion coefficient of  $\text{LaCrO}_3$  around structural transition at heating rates of 2, 5 and  $10 \text{ K min}^{-1}$ .

Table 2

Linear thermal expansion coefficient of  $\text{LaCrO}_3$  of the present study

$T$ (K)	$\alpha$ ( $10^{-6} \text{ K}^{-1}$ )	$T$ (K)	$\alpha$ ( $10^{-6} \text{ K}^{-1}$ )
100	3.32	480	7.32
120	3.84	500	6.71
140	4.48	520	0.81
160	5.15	529	-17.64
180	5.98	540	3.23
200	6.69	560	8.41
220	7.41	580	8.85
240	8.34	600	9.02
260	9.30	620	9.11
280	10.58	640	9.17
283	10.66	660	9.21
300	8.34	680	9.29
320	7.75	700	9.32
340	7.60	720	9.42
360	7.60	740	9.49
380	7.60	760	9.60
400	7.60	780	9.60
420	7.60	800	9.60
440	7.60	850	9.60
460	7.54		

and compared with the reference data [5,7,14,21,26] in Table 3, whose temperature regions were reported before and after the structural transition separately. The reported values of the orthorhombic region in [5,7,21] and those of the rhombohedral region in [14,26] are slightly different from our results as seen in Tables 2 and 3. The smaller values in the orthorhombic region in [5,21] are considered to be mainly due to the fact that the averaged temperature ranges

Table 3

Mean thermal expansion coefficient of  $\text{LaCrO}_3$  from the reference data

$T$ (K)	$\alpha$ ( $10^{-6} \text{ K}^{-1}$ )	Reference
350–450	7.5	[14]
580–730	8.7	[14]
RT–513	6.7	[5]
Rhombohedral region	9.2	[5]
RT–550	8.6	[7]
580–1000	9.7	[7]
100–520	7.7	[26]
530–1140	7.3	[26]
313–547	4.6	[21]
563–1325	9.4	[21]

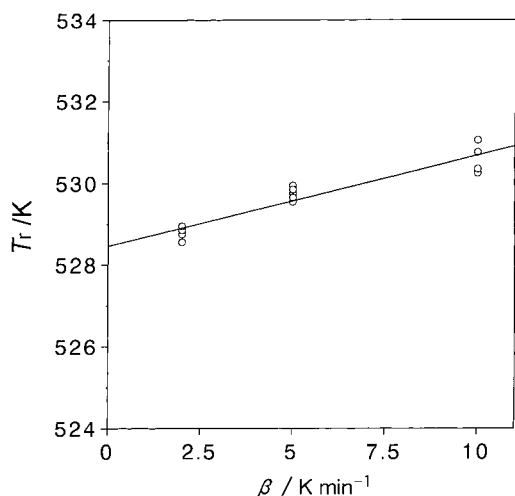


Fig. 6. Temperature of the structural phase transformation (minimum of  $\alpha$  vs.  $T$  curve) as a function of the heating rate  $\beta$ .

of [5,21] are extended to the regions of the phase transitions.

The magnetic transition of  $\text{LaCrO}_3$  is accompanied by a volume expansion as seen in Fig. 4. The temperature of the magnetic transition is 283 K regardless of the heating rates. The magnetic transition temperature of  $\text{LaCrO}_3$  was reported at 287 K by adiabatic calorimetry [7], 295 K [9] and 300 K [10] by static magnetic susceptibility, 295 K by electron paramagnetic resonance [11] and 320 K by neutron diffraction [8]. The reason for these differences is not clear, but may be due to sample preparation and the measuring method.

The structural transition is accompanied by a large volume shrinkage as seen in Figs. 4 and 5 as also reported by Tolochko et al. [14]. The temperature of the structural transition becomes higher with the increase of the heating rate as seen in Fig. 5. The transition temperature against the heating rate is shown in Fig. 6. The transition temperature is obtained to be  $528.5 \pm 0.5$  K by extrapolating the transition temperature to  $0 \text{ K min}^{-1}$ . The structural transition temperature of  $\text{LaCrO}_3$  was reported at 527 K by thermal expansion measurement [14], 536 K [7] and 547 K [16] by adiabatic calorimetry and 544 K by differential scanning calorimetry [21]. The present result is somewhat lower than that by calorimetry [7,16,21] but agrees with that by the thermal expansion measurement [14].

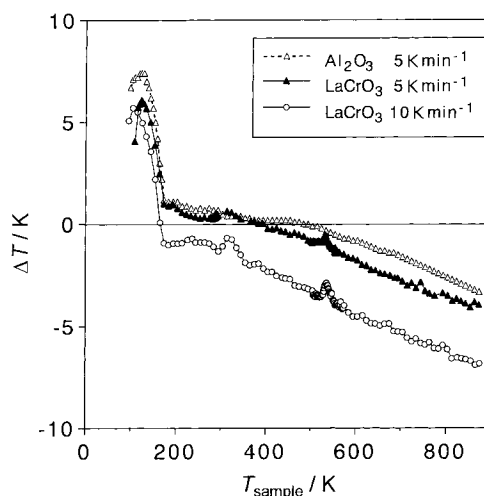


Fig. 7. Temperature difference  $\Delta T = T_{(\text{position B})} - T_{(\text{position A})}$  between the sample and the reference as a function of the temperature of the sample.

### 3.3. Influence of the position of thermocouple on the measurement of thermal expansion coefficient

As described in Eq. (3), one of the most important errors to measure the thermal expansion coefficient is dependent on the measurement of the temperature. In the push-rod type dilatometer, the temperature measured using the thermocouple set on the reference side like the position B in Fig. 1 is often regarded as the temperature of the sample. In such a case, it is important to know the error due to the difference of the temperature of the position B and the real temperature of the sample. The temperatures of the position A (sample) and the position B (reference side) were measured at the same time. The difference of the temperature between the sample and the reference side for  $\text{LaCrO}_3$  at the heating rate of 5 and  $10 \text{ K min}^{-1}$  and for  $\text{Al}_2\text{O}_3$  at the heating rate of  $5 \text{ K min}^{-1}$  are shown as a function of the temperature of the sample in Fig. 7. The large difference below 200 K shows that the larger heat capacity of the thermocouple which is bonded on the sample (position A) than the thermocouple set on the reference side (position B), as described in the experimental section. The temperature of the sample is lower at low temperatures and becomes higher than the reference as the temperature increases. This tendency can be explained as the delay of temperature rise due to the larger heat capacity of the sample

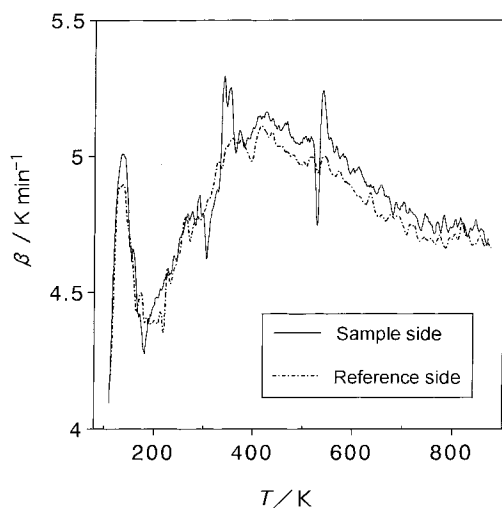


Fig. 8. Heating rates measured by the thermocouples set on the sample and the reference side for LaCrO<sub>3</sub> at a heating rate of 5 K min<sup>-1</sup>.

(position A) at low temperatures and the rapid temperature rise due to larger radiative heat transfer at high temperatures. Two small anomalies for LaCrO<sub>3</sub> around 300 and 500 K at each heating rate seen in Fig. 7 are due to the effects of the phase transitions. The difference of the temperature is approximated as a linear function of the temperature under the steady state heating above 300 K as seen in Fig. 7. It indicates that the heating rate of the reference is above 300 K slightly lower than that of the sample. The heating rate of the sample and that of the reference for LaCrO<sub>3</sub> at the heating rate of 5 K min<sup>-1</sup>, which was controlled using the thermocouple set at the furnace, are shown in Fig. 8 as the function of the temperature. The changes of the heating rate of the sample and the reference show similar tendency except for low temperatures and the regions of the phase transitions. The absolute values of the heating rate, however, became different each other under the steady state heating above 200 K. This difference results in the error of the thermal expansion coefficient, when the temperature was measured on the reference side. The heating rate of the reference side above 400 K is about 1% lower than that of the sample. The difference of the heating rate and the temperature difference as seen in Fig. 7 should be corrected in order to obtain the accurate thermal expansion coefficient, when the temperature was measured on the reference side. These corrections were

carried out as follows. The temperature of the reference side,  $T_{\text{ref}}$ , was corrected to the sample temperature,  $T_{\text{sam,corr}}$ , using

$$T_{\text{sam,corr}} = \Delta T(T_{\text{ref}}) + T_{\text{ref}}, \quad (6)$$

where  $\Delta T(T_{\text{ref}})$  means the polynomial equation fitted to the averaged temperature difference of LaCrO<sub>3</sub> and Al<sub>2</sub>O<sub>3</sub> at the heating rate of 5 K min<sup>-1</sup> as a function of the temperature of the reference side. The thermal expansion coefficient obtained by the temperature measured on the reference side,  $\alpha_{\text{ref}}$ , was corrected for each heating rate,  $\beta_{\text{ref}}$  and  $\beta_{\text{sam}}$ , to that on the sample side  $\alpha_{\text{sam,corr}}$ , using

$$\alpha_{\text{sam,corr}} = \alpha_{\text{ref}} \left( \frac{\beta_{\text{ref}}(T_{\text{ref}})}{\beta_{\text{sam}}(T_{\text{sam,corr}})} \right), \quad (7)$$

where  $\beta_{\text{ref}}(T_{\text{ref}})$  and  $\beta_{\text{sam}}(T_{\text{sam,corr}})$  are the heating rate measured by the thermocouple set on the reference side and the sample respectively. The heating rates,  $\beta_{\text{ref}}(T_{\text{ref}})$  and  $\beta_{\text{sam}}(T_{\text{sam,corr}})$  were obtained from least-square fits to the  $\beta$ - $T$  curves in Fig. 8, respectively. The thermal expansion coefficient of LaCrO<sub>3</sub> obtained by the temperature measurement on the reference side at the heating rate of 5 K min<sup>-1</sup> before and after the correction are shown in Figs. 9 and 10, where the thermal expansion coefficient obtained by the measurement on the sample side is also shown for

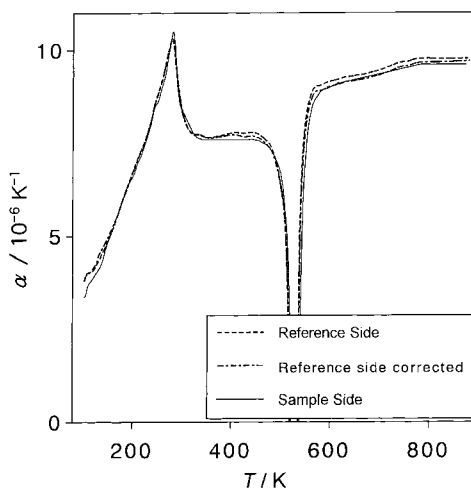


Fig. 9. Thermal expansion coefficient of LaCrO<sub>3</sub> measured by the thermocouple on the reference side at a heating rate of 5 K min<sup>-1</sup> and the corrected value compared with that measured by the thermocouple on the sample.

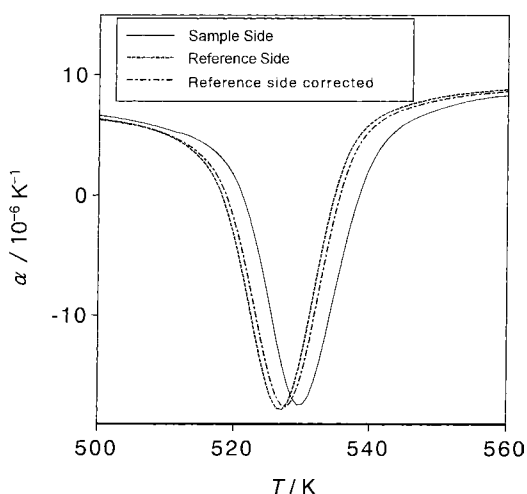


Fig. 10. Thermal expansion coefficient of  $\text{LaCrO}_3$  around the structural transition measured by the thermocouple on the reference side at a heating rate of  $5 \text{ K min}^{-1}$  and the corrected value compared with that measured by the thermocouple on the sample.

comparison. The thermal expansion coefficient when the temperature was measured on the reference side is about 1% higher than that on the sample and it approaches to that on the sample after the correction. The temperature of the structural transition obtained by the temperature measurement on the reference side, even after the correction, was 2 K lower than that obtained by the sample side at the heating rate of  $5 \text{ K min}^{-1}$  as seen in Fig. 10.

#### 4. Conclusions

Thermal expansion coefficients of  $\text{Al}_2\text{O}_3$  and  $\text{LaCrO}_3$  were measured in the temperature range from 100 to 873 K using a push-rod type dilatometer. The error depending on the position of the thermocouple in the dilatometer was also investigated.

1. The thermal expansion coefficient of  $\text{Al}_2\text{O}_3$  was measured in the temperature range from 100 to 873 K continuously by a single dilatometer and it was generally agreed with the literature.
2. The anomaly accompanying a volume expansion in the thermal expansion coefficient was observed in  $\text{LaCrO}_3$  at 283 K due to the magnetic transition from an anti-ferromagnetic to a paramagnetic state.

3. The anomaly accompanying a large shrinkage was observed at 528.5 K in  $\text{LaCrO}_3$  due to the phase transition from an orthorhombic to a rhombohedral structure.
4. The temperature difference between the thermocouples set on the sample and on the reference side increases with the temperature. The thermal expansion coefficient using the thermocouple on the reference side was about 1% higher than that using the thermocouple attached on the sample. The error comes mainly from the error of the heating rate resulting from the position of the thermocouple.
5. The transition temperature of  $\text{LaCrO}_3$  from the orthorhombic to the rhombohedral phase using the thermocouple set on the reference side was 2 K lower than that on the sample side at the heating rate of  $5 \text{ K min}^{-1}$ .

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