CRYSTAL STRUCTURE ANALYSIS OF LaCrO₃ SYSTEM

I. SPACE GROUP DETERMINATION BY CONVERGENT-BEAM ELECTRON DIFFRACTION

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ABSTRACT

Crystal system of LaCrO₃ was analyzed with selected area electron diffraction (SAED) and convergent-beam electron diffraction (CBED). All the reflection spots of SAED patterns of LaCrO₃ at room temperature could successfully be indexed as orthorhombic symmetry with primitive lattice of \(a=5.479\ \text{Å}, \ b=5.516\ \text{Å} \) and \(c=7.766\ \text{Å}\). The space group of LaCrO₃ at room temperature was determined to be \(Pbnm\) (No. 62) from the analysis of CBED patterns. The reflection spots of SAED patterns which indicated orthorhombic symmetry disappeared with increase of temperature up to 300°C. From CBED patterns, it was clarified that the crystal system of LaCrO₃ at 300°C was rhombohedral with space group of \(R3c\) (No. 167).

INTRODUCTION

For interconnect of solid oxide fuel cells (SOFC), material with high electrical conductivity and high endurance at temperatures as high as 1000°C under both oxidative and reductive atmospheres is desired. Sr- and/or Ca-substituted LaCrO₃ is one of the candidates for the material of interconnect of SOFC since it shows relatively high electrical conductivity and high stability under both oxidative and reductive atmospheres at high temperatures (1-3). Several problems, however, remain for the practical application of Sr- and/or Ca-substituted LaCrO₃ as a material for interconnect of SOFC. One of the problems is the first order structural phase transition of Sr- and/or Ca-substituted LaCrO₃ around 260°C (4). Since the molar volume of Sr- and/or Ca-substituted LaCrO₃ varies discretely at the transition temperature, internal stresses might generate and destroy the cell mechanically during the heat cycle for maintenance of SOFC.

For the solution of above problem, precise information on crystal structure of...
LaCrO$_3$ is essential. It has been reported that the crystal structure of LaCrO$_3$ is orthorhombic-distorted perovskite with the lattice constants of $\sqrt{2}a_p x \sim \sqrt{2}a_p y \sim 2a_p$, where $a_p$ is a lattice constant of pseudo-cubic perovskite structure, below the transition temperature (5). Also reported is the rhombohedral-distorted perovskite phase above the transition temperature (6). However, there have been few papers which refer to the space group, the most important information for the analysis of crystal structure. Khattak and Cox (5) and Berjoan and coworkers (7) reported that the space group of LaCrO$_3$ at room temperature is $Pbnm$ (No. 62) (7). Höfer and Kock reported that the space group of rhombohedral-distorted LaCrO$_3$ was $R3m$ (No. 166) (8). However, their proposed space group is not decisive since their conclusion was based upon a powder X-ray diffraction only. Direct observation of crystal symmetry is required to determine the space group.

Convergent-beam electron diffraction (CBED) is a powerful tool to determine the space group since direct observation of crystal symmetry can be carried out by this method (9). Tsuda and Tanaka succeeded in determination of space group of tetragonal-distorted perovskite, low temperature phase of SrTiO$_3$ by using CBED (10). In this study, the space group of LaCrO$_3$ at room temperature and at 300°C was determined.

**EXPERIMENTAL**

The LaCrO$_3$ polycrystalline powder was supplied by Nikkato Co., Ltd. The powder was pressed into pellet and sintered at 1200°C for 4 h in air. Almost all the powder X-ray diffraction peaks of the specimen could be indexed as orthorhombic symmetry with lattice constant of $a=5.479$ Å, $b=5.516$ Å and $c=7.766$ Å.

The specimen for CBED and selected area electron diffraction (SAED) was prepared by crushing the pellets and dispersing the fragments on a microgrid. The CBED and SAED were conducted using a JEM2010 or JEM2000FX electron microscope (JEOL Co., Ltd.) operated at 100kV equipped with LaB$_6$ emitter. The temperature for measurement was either room temperature or 300°C. The microgrid coated with silver was used for diffraction measurement at 300°C to improve thermal conduction.

**RESULTS AND DISCUSSION**

**SAED Patterns at Room Temperature**

Figure 1 shows SAED patterns of LaCrO$_3$ at room temperature taken from various incidences. All the reflection spots could be indexed assuming orthorhombic symmetry of $a=5.479$ Å, $b=5.516$ Å and $c=7.766$ Å. The spots indexed as 100, 010, 021 and 012 indicate that the lattice type of LaCrO$_3$ at room temperature is a primitive one.

**CBED Patterns at Room Temperature**

Figure 2(a) shows the CBED pattern of LaCrO$_3$ at room temperature taken from [010] incidence. Zero-th order Laue-zone (hereafter abbreviated to ZOLZ) reflections
were observed in the center of the pattern, which are enlarged in Figure 2(b). Since the position and the distribution of intensity of disks in ZOLZ reflection showed 2-fold rotation and two types of mirror symmetry, the symmetry of Figure 2(b) was $2\text{mm}$. Besides ZOLZ reflection, higher order Laue-zone (HOLZ) reflections appeared as rings surrounding the ZOLZ reflections. In Figure 2(a), HOLZ reflections and ZOLZ ones are presented. The symmetry of $2\text{mm}$ was also observed in HOLZ reflections. Therefore, the symmetry of whole pattern of CBED depicted in Figure 2(a) was concluded to be $2\text{mm}$.

Figure 1. SAED pattern of LaCrO$_3$ at room temperature. Incidence of electron (a) [001] (b) [010] (c) [100] (d) [021] (e) [110] (f) [111]

Figure 2. CBED pattern of LaCrO$_3$ at room temperature taken from [010] incidence. (a) whole pattern (b) ZOLZ reflection pattern. m indicates mirror perpendicular to the surface.
Figure 3(a) shows the CBED pattern of LaCrO3 at room temperature taken from [001] azimuth. ZOLZ reflections were observed in the center of the pattern, which were enlarged in Figure 2(b). The symmetry of whole pattern of CBED depicted in Figure 3(a) was also 2mm. Since both patterns of CBED taken from [010] incidence and that from [001] azimuth showed symmetry of 2mm, the point group of LaCrO3 at room temperature was determined to be mmm (9).

The white lines, indicated by arrows in Figure 3(b), were observed in the ZOLZ reflection disks indexed as $h00$ where $h$ was odd number. This white line, which is called GM line, indicates there is screw axis and/or glide plane exist in the crystal (9, 11). The GM line was also observed in the ZOLZ reflection disk indexed as $0k0$ where $k$ was odd number. Among CBED patterns, taken from [001] azimuth, of specimens with primitive lattice and point group of mmm, only CBED pattern of the specimen with space group of Pbnm (No. 62) shows GM line in both $h00$ and $0k0$ ZOLZ reflection disks (12). Therefore, it was determined that the space group of LaCrO3 at room temperature was Pbnm (No. 62).

**SAED Patterns at 300°C**

Figure 4(a) and Figure 5(a) show SAED patterns of LaCrO3 at room temperature taken from [021] and [112] incidence, respectively. All reflection spots could be indexed as orthorhombic symmetry. Some of the reflection spots disappeared with increase of temperature up to 300°C as Figure 4(b) and Figure 5(b) show, suggesting structural phase transition between room temperature and 300°C. The SAED pattern of LaCrO3 at 300°C could be indexed as rhombohedral symmetry with $a=5.484$ Å and $c=13.165$ Å, showing agreement with the preceding study (6, 8). Here, we employ hexagonal lattice for description of rhombohedral symmetry for convenience.

![Figure 3](image)

**Figure 3.** CBED pattern of LaCrO3 at room temperature taken from [001] incidence. (a) whole pattern (b) ZOLZ reflection pattern. m indicates mirror perpendicular to the surface. GM line is indicated by arrows.
Figure 4. SAED pattern of LaCrO$_3$ at (a) room temperature and (b) at 300°C. Incidence of electron is [021] of orthorhombic lattice i.e. [001] of hexagonal lattice. The reflection spots indicated by arrows are derived from orthorhombic lattice.

Figure 5. SAED pattern of LaCrO$_3$ at (a) room temperature and (b) at 300°C. Incidence of electron is [1T2] of orthorhombic lattice i.e. [110] of hexagonal lattice. The reflection spots indicated by arrows are derived from orthorhombic lattice.

**CBED Patterns at 300°C**

Figure 6 depicts one of the CBED patterns of LaCrO$_3$ at 300°C taken from c-axis direction of hexagonal lattice. HOLZ reflections and ZOLZ ones are enlarged in Figure 6(a) and 6(b), respectively. The symmetry of HOLZ reflections was 3$m$ since 3-fold rotation and three kinds of mirror were observed in HOLZ reflections. The projection diffraction group, which could be obtained from symmetry of only ZOLZ reflections, was 6mm1$R$ since 6-fold rotation and two types of mirror were observed in ZOLZ reflections. Therefore, diffraction group of CBED pattern depicted in Figure 6 was 6$RmmR$ (9, 13). Since the point group which shows CBED pattern with diffraction group of 6$RmmR$ is either 3$m$ or m3$m$ (9) and SAED pattern of LaCrO$_3$ at 300°C could not be indexed as cubic symmetry, the point group of LaCrO$_3$ at 300°C could be determined to be 3$m$.
Figure 7 shows CBED pattern of LaCrO$_3$ at 300°C taken from [1\bar{1}0] incidence. Observed was the GM line in 00$l$ reflection disks of ZOLZ where $l$ equals to 6$n$+3, indicating that $c$-glide plane existed in the crystal. Besides GM line, observed in whole pattern of CBED was a mirror which indicated that $c$-glide plane included direction of electron incidence. Thus, the space group of LaCrO$_3$ at 300°C was determined to be $R\overline{3}c$ (No. 167).

**Figure 6.** CBED pattern of LaCrO$_3$ at 300°C taken from [001] of hexagonal lattice. (a) whole pattern. HOLZ reflections are enlarged. (b) ZOLZ reflections.

**Figure 7.** CBED pattern of LaCrO$_3$ at 300°C taken from [1\bar{1}0] of hexagonal lattice. (a) whole pattern (b) ZOLZ reflections. Arrows indicate GM-line observed in disks of ZOLZ reflection.
The ideal cubic perovskite, ABX₃, is composed of three dimensional network of regular corner-linked BX₆ octahedra and A cations located in the spaces between them. The majority of distorted perovskites are derived from the cubic aristotype by the practically rigid tilting of the octahedral units. According to Glazer (14), it is convenient to describe octahedral tilting in terms of component tilt around pseudo-cubic axes. Glazer described the tilting using symbols of the type $\tilde{a}b\tilde{c}$, in which the literal refer to tilts around the [100], [010] and [001] directions of the pseudo-cubic lattice and the superscript # takes the value 0, + or - to indicate no tilt around the axis or tilts of successive octahedra in the same or opposite sense. Letters are repeated to indicate equal tilts around the different pseudo-cubic axes. For example, Figure 8 shows a view from [001] direction of two adjacent layers of octahedra for (a) the $\tilde{a}\tilde{a}\tilde{c}$ tilt system and (b) the $a^0a^0c^+$ tilt system (15).

Glazer found that the crystal structure with space group of $Pbnm$ (No. 62) and $R3c$ (No. 167) appeared in distorted perovskite by tilts of octahedra as $a'b'a'$ and $a'a'a'$, respectively (14), which was recently confirmed by Woodward (15) and Howard and Stokes (16). Although more studies to determine the atomic position by using neutron-diffraction and so on is necessary, we conclude that the crystal structure of LaCrO₃ at room temperature and at 300°C is distorted perovskite denoted as $a'b'a'$ and $a'a'a'$, respectively.

**SUMMARY**

The space group of LaCrO₃ at room temperature and at 300°C was determined to be $Pbnm$ (No. 62) and $R3c$ (No. 167), respectively, by using selected area electron diffraction and convergent-beam electron diffraction. It is concluded that the distortion from ideal perovskite structure of LaCrO₃ can be expressed as $a'b'a'$ and $a'a'a'$ at room temperature and at 300°C, respectively.
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