Phase-transformation-induced twins in pressureless-sintered lanthanum gallate (LaGaO$_3$) ceramics have been analyzed using transmission electron microscopy. Twins are induced by solid-state phase transformation upon cooling from rhombohedral ($r$, $R3c$) to orthorhombic ($o$, $Pnma$) symmetry at 145°C. Domains with a 150°–60°–150° configuration were frequently detected when viewed along [210]. This observation representing the co-existence of the {121} and {123} twins is suggested by analyzing corresponding selected area diffraction patterns across the domain boundaries. The former, with the twin plane lying on {121}, is the reflection type whose twin variants are related by mirror plane symmetry. The latter, although its nature was confirmed by tilting experiments along an unsplit row of reflections, exhibits characteristic crystallographic orientation relationships that are distinctive from those of the {121} twins. The twin laws represented in the matrix form are also derived accordingly from corresponding orientation relationships. Crystallographic analysis indicates that these domains commonly possess an orientation relationship that can be described by the twofold rotation axis about {111} lost upon the rhombohedral → orthorhombic phase transition. They are therefore the 180° parallel-rotation twin, with the twin axis {111} lying in {123}. Twins generated by the $r$ → $o$ phase transition between crystals of non-group–subgroup relations are discussed in terms of an intermediate metastable cubic phase of the lowest common supergroup symmetry.

I. Introduction

Lanthanum gallate perovskite (LaGaO$_3$) with lattice spacing and thermal expansion matching closely with YBa$_2$Cu$_3$O$_{7-\delta}$, is a good substrate suitable for high-temperature superconductor films. Recently, doping with strontium and magnesium, (La,Sr)(Ga,Mg)O$_3$ (LSGM), has also been developed for new application as an oxide ionic electrolyte in solid-oxide fuel cells. LaGaO$_3$ perovskite is orthorhombic ($o$) under ambient conditions and transforms to rhombohedral ($r$) upon increasing either the temperature or pressure. It was reported that LaGaO$_3$ undergoes a first-order phase transition from rhombohedral ($R3c$ (No. 167)) to orthorhombic ($Pnma$ (No. 62)) at 145°C upon decreasing temperature. Such a temperature-driven transition is accompanied with twin domains that have been well characterized for LaGaO$_3$ in single-crystal form. Two major types of reflection twins with twin planes lying in {121} and {101}, induced on the phase transition to orthorhombic $Pnma$ symmetry, have also been reported for LaGaO$_3$ ceramics, as well as other ABO$_3$ perovskites, e.g., CaTiO$_3$, MgSiO$_3$, LaMnO$_3$, and NdGaO$_3$. Twins generated upon phase transformation are attributed to point group symmetry element(s) reduction from a higher symmetry phase to a lower symmetry one. The lost symmetry element may be a mirror plane, a rotation axis, or an inversion center. The lost plane symmetry (i.e., mirror plane) by which the crystallographic orientations of both crystal parts are related becomes a reflection twin. On the other hand, a rotation twin is produced upon losing reflection symmetry (i.e., rotation axis) and the crystal parts are related by the operation of a rotation axis (usually twofold). Nevertheless, the rotation twin characterized by 180° rotation about the twin axis does not suggest that it is formed physically by such a rotation with respect to each other. Instead, it merely states the orientation relationship between the two crystal parts generated upon polymorphic phase transition.

LaGaO$_3$ at room temperature and under atmospheric pressure is isostructural with the GdFeO$_3$ type ($Pnma$, $Z = 4$) which is a distorted perovskite resulting from octahedral tilting. The crystal structure is usually constructed on the framework of pseudo-cubic unit cell, as shown in Fig. 1(a). Figures 1(b) and (c) illustrate schematically the spatial orientation relationships of the (121), and (101)$_o$ orthorhombic twin planes. For convenience, the subscript $o$ representing orthorhombic planes and directions is omitted hereafter. Both twins related by a mirror operation across the respective twin plane are the reflection type. The (121) twins were identified by examining along the {101} or {210} zone axes, while the {101} appeared edge-on when looking from the orthorhombic axes. Their being the reflection type has further been confirmed by tilting experiments in a transmission electron microscope (TEM).

Phase-transformation-induced twins in sintered LaGaO$_3$ ceramics were investigated previously from a crystal symmetry perspective using TEM. Additional twins lying on {123} not reported before are found in the present study. In contrast to the reflection type, the {123} twins are the (111) 180° parallel-rotation type as distinguished by the crystallographic orientation relationships determined by TEM.

II. Experimental Procedures

A stoichiometric LaGaO$_3$ powder was prepared by reacting La$_2$O$_3$ (99.9% pure, Meldform Metals, Royston, U.K.) with Ga$_2$O$_3$ (99.9% pure, Meldform Metals) at a 1:1 molar ratio in solid state by mixed oxides technique. La$_2$O$_3$, easily hydrolyzed to form La(OH)$_3$, was calcined at 1000°C for 2 h in air before weighing. It was then mixed with Ga$_2$O$_3$ in a ball mill with acetone using yttria-stabilized ZrO$_2$ balls in a polyethylene bottle for 24 h. After being dried at 90°C for 48 h, ground using an agate mortar and pestle, and de-agglomerated by sieving through a 150 μm mesh, the powders were calcined at 1000°C for 4 h and de-agglomerated again before being pressed into disks of 10 mm diameter using a WC-inserted steel die at a uniaxial pressure of 35 MPa. The disks were sintered in air at 1500°C for 4 h at the heating and cooling rate of 5°C/min.

The microstructure was characterized using a JEOL™ AEM 3010 (Tokyo, Japan) operating at 300 kV. As-sintered disks (of ~1200 μm thick) were ground on both sides to approximately half the thickness before being polished on one side using diamond lapping films (3M, St. Paul, MN) successively to ~1 μm surface roughness and reduced to ~300 μm thickness. Mounted
The domains were all indexed to an identical zone axis [210], but they differed in the c-axis direction across adjacent domains boundaries, as shown in Figs. 2(a)–(d) and indicated by arrows in Fig. 2(e). The 001 reflections belonging to kinematically forbidden reflections 0kl with k+l= odd and allowing reflections of 00l with l = even, e.g., 001 and 003, have emerged dynamically from all domains. The variation of the c axis resulted from loss of the threefold symmetry, producing twin variants upon phase transition from rhombohedral (R3c) to orthorhombic (Pnma) symmetry. The viewing direction [210] corresponds to [111], of the high-temperature rhombohedral phase. The rhombohedral threefold axis [111], (i.e., 3 in R3c) was suppressed upon the \(r \rightarrow o\) phase transition when the temperature was decreased. This consequently generated three orientation variants in the transformation twin domains. The +c axis in domains \(A_1-B_1-C_1\) and \(A_1-B_1-D_1\), as shown by arrows in Fig. 2(e), subtending a 120° angle between any two neighboring domains, represent three orientation variants. However, such a domain configuration of 120°–120°–120° converging to a triple point has not been observed in the present samples, although a similar feature was observed and its existence in (La,Sr)MnO3 as suggested by Déchamps et al.13,14 Instead, the boundaries of domains \(A_1-B_1-C_1\) at a triple junction have exhibited 60° and 150° angle between two adjacent twin boundaries, as indicated in Fig. 2(e).

Twin planes in this grain were determined by comparing BF image and the corresponding SADP, following the same procedures as described before, i.e., examining the existence of the unsplit row of reflections (USR) and the direction of spot splitting. They are determined according to \((123)_{A_1}\) or \((123)_{B_1}\), for domain boundary \(A_1-B_1\), \((123)_{B_2}\) or \((123)_{C_1}\) for domain boundary \(B_1-C_1\), and \((121)_{A_1}\) or \((121)_{C_2}\) for domain boundary \(A_1-C_1\). Both the \([121]\) and \([123]\) twin planes have co-existed in domains \(A_1-B_1-C_1\). Nevertheless, confirmation of such domains being the reflection type requires tilting about USR.

Figure 3(d) shows another grain with boundaries converged to a triple junction. Such domain configurations were commonly observed in sintered LaGaO3. They are designated \(A_2, B_2, A_3, B_3\,\) and \(C_3\,\) and corresponding SADPs are shown in Figs. 3(a), (b), and (c), respectively. The twin boundaries that exhibited no fringe contrast and appeared in an edge-on condition were viewed along Z = [210], similar to that observed in domains \(A_1-B_1-C_1\) (Fig. 2). The +c-axis in domains \(A_2, B_2,\) and \(C_2\,\) as shown by the arrows in Fig. 3(d), were inclined at an angle of 120° between each other, also similar to domains \(A_1-B_1-C_1\) (Fig. 2).

The three domain boundaries \(A_2-B_2, B_2-C_2,\) and \(A_2-C_2\) were determined for a twin plane by SADPs obtained from across the respective twin boundary as shown in Figs. 3(e), (f), (g), (h), and (i).
and 4(a), respectively. The USR from domains A$_2$–B$_2$ appears in the direction parallel to 121$_{A_2}$ and 121$_{B_2}$, and that from B$_2$–C$_2$ domains also lies along 121$_{B_2}$ and 121$_{C_2}$. This has also been confirmed from the high-order reflections, e.g., 363$_{A_2}$ and 363$_{B_2}$, and 363$_{C_2}$, as shown in the inset of Figs. 3(e) and (f). As a result, both A$_2$–B$_2$ and B$_2$–C$_2$ domains are the {} twin, and the spot splitting is parallel to USR along 121$_{A_2}$, as shown in the inset in Figs. 3(e) and (f).

Figure 4(a) shows SADP contributed by both domains A$_2$ and C$_2$ (Fig. 3(d)) in which USR has appeared along 121$_{A_2}$ and 123$_{C_2}$. The coincident lattices were confirmed by investigating high-order reflections, e.g., 246$_{A_2}$ and 246$_{C_2}$, as indicated and shown in the inset of Fig. 4(a), suggesting that the twin plane lies in the 123$_{A_2}$ and 123$_{C_2}$. Other reflection rows exhibited spot splitting, indicated by 363$_{A_2}$ and 363$_{C_2}$, also shown in the inset, whose direction was parallel to the 123$_{A_2}$ USR. The characteristics similar to those observed in the regions and } twin suggest that they are the reflection type.$^{13,14}$

Domains A$_2$–B$_2$–C$_2$ (Fig. 3(d)), similar to domains A$_1$–B$_1$–C$_1$ (Fig. 2(e)), also have domain boundaries of a 150°–60°–150° configuration with the +c-axis inclining 120° mutually, as indicated by arrows, when viewing from [210]. The {121} and {123} twins again co-existed.

(2) Tilting Experiments on the {123} Twin

Similar to {121} and {101}$^{13,14}$ tilting experiments$^{30,31}$ were performed to determine the type of the {123} twin.

Figure 4(b) shows SADP obtained while tilting the crystal about the direction perpendicular to USR (denoted USR$_||$). The 123$_{A_2}$ twin plane has become slightly inclined to the electron beam. Examining the high-order reflections along 121$_{A_2}$, e.g., 246$_{A_2}$ of domain A$_2$ and 246$_{C_2}$ of domain C$_2$, as indicated and shown in the inset in Fig. 4(b), only one coincident spot has appeared. This suggests that 123$_{A_2}$ is a common plane to domains A$_2$ and C$_2$. Spot splitting occurred in other rows, e.g., 363$_{A_2}$ and 363$_{C_2}$, as indicated and shown in the inset in Fig. 4(b), where the direction of splitting was still parallel to the 123$_{A_2}$ USR and the magnitude of splitting increases with the distance to USR. Similarly, Fig. 4(c) shows SADP obtained by tilting the crystal counterclockwise about the direction parallel to USR (denoted USR$_\perp$), where the direction of splitting was still parallel to the 123$_{A_2}$ USR and the magnitude of splitting increases with the distance to USR.

![Fig. 3. {123} twins co-existing with {121} twins (d) when viewed from Z = [210] with corresponding selected area diffraction patterns ((a)–(c)), and (e)–(f) showing corresponding selected area diffraction patterns of domains A$_2$–B$_2$ and B$_2$–C$_2$, respectively.](image1)

![Fig. 4. Tilting experiment on the {123} twins (domains A$_2$–C$_2$), showing the corresponding selected area diffraction patterns that are (a) in zone, (b) perpendicular to unsplit row of reflection (USR$_\perp$), and (c) parallel to USR (USR$_||$).](image2)
were still coincident and the other rows were split in the same direction parallel to the \( \text{USR} \), as shown in the inset in Fig. 4(c). Therefore, the \{123\} twin, which exhibited similar reflection characteristics as the \{121\} and \{101\} twins,\textsuperscript{13,14} appears to be the reflection type where only one row of unsplit spots exists and the spot splitting remains parallel to the \( \text{USR} \).\textsuperscript{30,31}

**IV. Discussion**

The transformation twins, both of the reflection type, lying in \{121\} and \{101\} planes induced upon phase transition were identified in single-crystal\textsuperscript{8–12} and polycrystalline LaGaO\(_3\)\textsuperscript{13,14}. The co-existence of \{121\} and \{123\} twins in LaGaO\(_3\) grains observed here has enabled to differentiate the reflection twin of the former from the 180° parallel-rotation twin of the latter unambiguously.

**3. Parallel Zone Axes Between Domains \( A_2-B_2 \) and \( A_2-C_2 \)**

Tilting domain \( A_2 \) along the \( \{121\}_A \), Kikuchi pair while keeping twin plane edge-on and parallel to the electron beam, four parallel zones have been observed between domains \( A_2 \) and \( B_2 \). Domains \( A_2 \) and \( B_2 \) have mutually parallel crystallographic directions exist, i.e., \( [111]_A || [111]_B \), \( [321]_A || [321]_B \) (Figs. 5(a) and (d)), \( [210]_{A2} || [210]_{B2} \) (Figs. 5(b) and (e)), and \( [311]_A || [311]_B \) (Figs. 5(c) and (f)). Corresponding twin relations of domains \( A_2 \) and \( B_2 \) represented by mirror plane \{121\} are indicated in SADPs (Figs. 5(a)–(f)). Similarly, parallel zone axes between domains \( A_2 \) and \( C_2 \) were identified by tilting along the \( \{123\}_A \) trace. This is shown in Figs. 6(a) to (f) where mutually parallel crystallographic directions, i.e., \( [121]_A || [301]_C \) (Figs. 6(a) and (d)), \( [210]_A || [210]_C \) (Figs. 6(b) and (e)), and \( [301]_A || [121]_C \) (Figs. 6(c) and (f)). However, no mirror plane in domains \( A_2 \) and \( C_2 \) from corresponding SADP (Figs. 6(a)–(f)) could be successfully assigned.

**1. Crystallographic Orientation Relationships of the \{121\} and \{123\} Twins**

The orientation relationships of both the \{121\} and \{123\} twins can be determined by plotting corresponding stereographic projections. Those of the \{121\} \( A_2-B_2 \) twin are illustrated schematically in Fig. 7(a), with all parallel zones identified experimentally shown in Figs. 5(a)–(f). The stereographic projections for domains \( A_2 \) and \( B_2 \) (Fig. 3(d)) sharing a twin plane \( \{121\}_A \) (or \( \{121\}_B \)) are superimposed with the parallel directions of \( [210]_A \) and \( [210]_B \) at the center of a great circle. Although \( [210] \) and the other directions of domains \( A_2 \) and \( B_2 \) were in parallel, the \( c \) axes (i.e., reciprocal direction \( 001^*_A \)) were not. The + \( c \) axis of domain \( B_2 \) was rotated counterclockwise about \( [210] \) by 120°, as indicated in Fig. 7(a) and this is indeed consistent with what has been found experimentally in Figs. 3(a) and (b).
The crystallographic orientation relationships describing the \{121\} twin law can be represented by a transformation matrix written in column matrix form. Transformation from \(\frac{1}{2}uvw/C138\) to \(\frac{1}{2}UVW/C138\) derived from the parallel directions is described by the following equation:

\[
\begin{bmatrix}
U \\
V \\
W
\end{bmatrix} =
\begin{bmatrix}
\frac{1}{2}
& 1
& -1 \\
\frac{1}{2}
& 0
& 1 \\
\frac{1}{2}
& -1
& 1
\end{bmatrix}
\begin{bmatrix}
u \\
v \\
w
\end{bmatrix}_{A2}
\]

The transformation matrix \(M_{A2\rightarrow B2}\) between \(\frac{1}{2}uvw/C138\) and \(\frac{1}{2}UVW/C138\) can then be written as

\[
M_{A2\rightarrow B2} =
\begin{bmatrix}
\frac{1}{2}
& 1
& -1 \\
\frac{1}{2}
& 0
& 1 \\
\frac{1}{2}
& -1
& 1
\end{bmatrix}
\]

For the crystallographic orientation relationships of the \{123\} twins, similar procedures are also used to derive twin law. The superimposed stereographic projections are again illustrated schematically in Fig. 7(b). The +c-axis of domains \(A_2\) and \(C_2\) are related by rotating 120° clockwise about [210] where coincident lattices of two crystal parts occur, as again evidenced experimentally in Figs. 6(a)–(f), and indicated in Fig. 7(b). The transformation matrix \(M_{A2\rightarrow C2}\) between \(\frac{1}{2}uvw/A2\) and \(\frac{1}{2}UVW/C2\) is therefore

\[
M_{A2\rightarrow C2} =
\begin{bmatrix}
\frac{1}{2}
& 1
& -1 \\
\frac{1}{2}
& 0
& 1 \\
\frac{1}{2}
& -1
& 1
\end{bmatrix}
\]

(2) 180°-Rotation Twins—Parallel Twins and Normal Twins

Although tilting experiments (Fig. 4) have indicated that the \{123\} twin is the reflection type, no mirror plane has been identified from the crystallographic orientations between corresponding SADPs (Fig. 6(a)–(f)). Accordingly, whether the \{123\} twin is a reflection type is not yet confirmed, and so far they cannot be regarded as such crystallographically.

The crystallographic orientation relationships for variants \(A_2\) and \(B_2\) (Figs. 3 and 5) have confirmed that crystal parts \(A_2\) and \(C_2\) sharing the \(\{121\}_{A2}\) common plane are variants of the \{121\] reflection twin. The crystallographic orientations of neighboring domains can be brought into coincidence by a reflection operation across the \{121\] twin plane, as shown in Fig. 1(b) and demonstrated experimentally in Fig. 5(a)–(f).
In domains A2–C2 (Fig. 3), crystal part A2 is also related to adjacent crystal part C2 by common plane $(1/2/1/1)_{A2}$. On tilting along the $(1/2/1/1)_{A2}$ trace, however, it was found that parallel zones did not belong to the same group of directions, i.e., $(11/1/1)_{A2} || (30/1)_{C2} \parallel (30/1)_{A2} || (12/1)_{C2}$ and $(11/1/1)_{A2} || (20/1)_{C2} \parallel (12/1)_{C2}$, are not related by mirror symmetry along the $(1/2/1/1)_{A2}$ trace. That is to say, the crystallographic orientation of variant A2 cannot be brought into coincidence with those of variant C2 by a mirror operation across the $(1/2/1/1)_{A2}$ twin plane. Therefore, unlike the $(121)$ twin, $(123)$ cannot be regarded as the reflection type.

Considering then for two possibilities of the $180^\circ$ rotation twins: (a) $180^\circ$ rotation about $(210)_{A2} - (210)_{C2}$, and (b) $180^\circ$ rotation about $(11/1/1)_{A2}$, the $180^\circ$ rotation about $(210)$ can be ruled out as the orthorhombic cells from variants A2 and C2 are not in accordance with the observation of their sharing $(123)_{A2}$, and +c-axis at $120^\circ$ mutually (Fig. 3) after such symmetry operation (as depicted schematically in Fig. 8(a) and (b)). However, if the orthorhombic cell of variant A2 is rotated by $180^\circ$ about $(11/1/1)_{A2}$, which is perpendicular to $(210)$ (as indicated in Fig. 8(a)), it coincides completely with that of variant C2 and results in the crystallographic orientation relationships correspondingly. Consistent with Figs. 6 and 7(b), the crystallographic orientations for variants A2 and C2 in a perspective view are illustrated schematically in Fig. 9(a) where crystal part (variant A2) on one side of the $(123)$ twin plane would then become identical to that (variant C2) on the opposite side of $(123)$ after a $180^\circ$ rotation about $(11/1/1)_{A2}$. The crystallographic accordance by a $180^\circ$ rotation about $(11/1/1)_{A2}$ suggests that $(123)$ is the $(111)$ $180^\circ$-rotation twin with rotation axis $(111)_{A2}$ lying on twin plane $(1/2/1/1)_{A2}$.

**Fig. 7.** (a) stereographic projection for 121 twins (domains A2–B2) and (b) that for 123 twins (domains A2–C2), showing the crystallographic orientation relationships.

**Fig. 8.** Perspective stereographic projections illustrating the orthorhombic unit cells of variants A2 (a) and C2 (b), according to the crystallographic orientations.
with the twin axis lying in twin plane $\{123\}$. Examine Fig. 7(a) for the $\{121\}$ twins; it is found that tilting along $\{111\}_{A_1}$, perpendicular to $\{210\}$, also brings about the coincidence of two crystal parts $A_2$, $B_2$ sharing the $\{121\}$ twin plane. Therefore, the $\{121\}$ reflection twins may also be perceived as the $\{111\}$ 180°-rotation twins, as depicted in Fig. 9(b). However, they are distinctively normal twins where the twin axis is perpendicular to the $\{121\}$ twin plane (Fig. 9(b)), only that the 180°-rotation twins in centrosymmetric crystals of orthorhombic $Pnma$ are equivalent to the reflection twins crystallographically.

(3) Group–Subgroup Relations

The $R_3c \rightarrow Pnma$ phase transition where group–subgroup relations do not exist is not second order in nature, although it is often found in perovskites with rare-earth cations at the A site, e.g., $LaGaO_3$, $LaMnO_3$, and $LaCrO_3$. The Landau theory forbids the first-order $r \rightarrow o$ transition in $LaGaO_3$ exhibiting twinning relationships between differently oriented domains of a lower-symmetry structure when structural coherence is lost between phases. The crystallographic origin of transformation-induced twins has been discussed, from loss or gain of symmetry elements for the $r \rightarrow o$ in $LaGaO_3$. Such treatments were based on the argument that phase transitions may be continuous and diffusionless if there is an intermediate phase of metastable nature that permits them to occur via second-order. The intermediate phase is either of the highest subgroup (monoclinic $P2_1/c$ (No.14)) or the lowest subgroup (cubic $Pm3m$ (No. 221)) symmetry common to the two end phases. The twin variant, twin laws derived accordingly for the low-symmetry orthorhombic phase (as shown in Table I) are indeed consistent with experimental observations, i.e., $\{121\}$, $\{101\}$, $\{010\}$, and now $\{123\}$ found here.

V. Conclusions

Phase-transformation-induced twins in pressureless-sintered $LaGaO_3$ ceramics of both the reflection and rotation types have been analyzed under TEM. The twin laws for both the $\{121\}$ and $\{123\}$ twins represented in matrix form are determined from corresponding crystallographic orientation relationships. The $\{121\}$ twin is the reflection type where twin variants are related by a mirror symmetry operation. However, the $\{123\}$ twin is a 180°-rotation twin with the $\{111\}$ twin axis lying in the $\{123\}$ twin plane.

Table I. Transformation Twins Predicted on the Basis of an Intermediate Cubic Phase Between the $r \rightarrow o$ Phase Transition

<table>
<thead>
<tr>
<th>Rhombohedral (32/m)</th>
<th>Cubic (4/m32/m)</th>
<th>Orthorhombic (2/m2/m2/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>${111}$</td>
<td>${111}$</td>
<td>Three orientation variants along ${210}$</td>
</tr>
<tr>
<td>${2/m}$</td>
<td>${010}$</td>
<td>${101}$</td>
</tr>
<tr>
<td>Gain $2/m$</td>
<td>${011}$</td>
<td>${101}$</td>
</tr>
<tr>
<td>Gain $4/m$</td>
<td>${100}$</td>
<td>${100}$</td>
</tr>
</tbody>
</table>

References


