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Twinning induced by the rhombohedral to orthorhombic phase transition in lanthanum gallate (LaGaO₃)

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Abstract Phase-transformation-induced twins in pressureless-sintered lanthanum gallate (LaGaO₃) ceramics have been analysed using the transmission electron microscopy (TEM). Twins are induced by solid state phase transformation upon cooling from the rhombohedral (*r*, $R\bar{3}c$) to orthorhombic (*o*, *Pnma*) symmetry at ~145°C. Three types of transformation twins {101}_o, {121}_o, and {123}_o were found in grains containing multiple domains that represent orientation variants. Three orthorhombic orientation variants were distinguished from the transformation domains converged into a triple junction. These twins are the reflection type as confirmed by tilting experiment in the microscope. Although not related by group–subgroup relation, the transformation twins generated by phase transition from rhombohedral to orthorhombic are consistent with those derived from taking cubic *Pm* $\bar{3}$ *m* aristotype of the lowest common supergroup symmetry as an intermediate metastable structure. The *r* → *o* phase transition of first order in nature may have occurred by a diffusionless, martensitic-type or discontinuous nucleation and growth mechanism.

Keywords Perovskite · LaGaO₃ · Phase transition · Twins

Introduction

Structural phase transitions in many ABO₃ perovskites are accompanied by twinning, which have been well characterized for CaTiO₃ (Kay and Bailey 1957; White et al. 1985; Hu et al. 1992; Wang and Liebermann 1993), MgSiO₃ (Wang et al. 1990, 1992), LaMnO₃ (Shibahara

et al. 1996; Arao et al. 2000; Déchamps et al. 2000; Ueno et al. 2005), LaGaO₃ (Wang et al. 1991; Yao et al. 1991; Fink-Finowicki et al. 1992; Bdikin et al. 1993; Dudley and Yao 1993), NdGaO₃ (Ubizskii et al. 1994; Uecker et al. 1994), and LaAlO₃ (Berkstresser et al. 1991; Yao et al. 1992; Norton and Biggers 1995; Kim et al. 2001). Most of them are orthorhombic (*o*) *Pnma* (No. 62) at ambient conditions, except for LaAlO₃ that is rhombohedral. Upon increasing temperature, the perovskites with orthorhombic symmetry at room temperature transform into rhombohedral (*r*) $R\bar{3}c$ (No. 167) for LaGaO₃, LaMnO₃, and NdGaO₃, and tetragonal (*t*) for CaTiO₃ and also MgSiO₃, in which the tetragonal phase transforms further into cubic (*c*). It is thought that all ABO₃ perovskites will eventually transform into cubic symmetry (*Pm* $\bar{3}$ *m*, No. 221) of the *aristotype* (Glazer 1975) upon further increase of temperature, assuming that melting or decomposition does not occur before the phase transition (Wang et al. 1990, 1992; Wang and Liebermann 1993). Although the two transformation sequences (i.e., *c* → *t* → *o* or *r* → *o*) are distinct, the twin relations in the orthorhombic *Pnma* symmetry are identical. Twins on {101}_o and {121}_o have often been reported for the low-temperature orthorhombic phase. While the subscripts for other structures are specified, the subscript *o* representing orthorhombic is omitted hereafter.

Various microstructure features such as twin domains, antiphase domains, and inversion domains are generated upon phase transitions that involve a change in space group symmetry (Nord 1992, 1997). Most frequently, the low-temperature phases have lower symmetry than the high temperature ones. When the low symmetry phase is a subgroup of the high symmetry one, symmetry-breaking transitions produce domain microstructures whose characteristics can be predicted by investigating the space group relationships between the high symmetry and low symmetry phase (Nord 1992, 1997). For example, the phase transition sequence of CaTiO₃ and MgSiO₃ is symmetry breaking from cubic (point group 4/ $m\bar{3}2/m$), to tetragonal (point group

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$4/m2/m2/m$), then to orthorhombic (point group $2/m2/m2/m$) upon lowering temperature. The orthorhombic twins with twin planes lying on $\{121\}$ were formed because of loss of the threefold symmetry ($\bar{3}$) upon the $c \rightarrow t$ transition, and those on $\{101\}$ loss of the fourfold symmetry (4) upon the $t \rightarrow o$ transition (Wang et al. 1990, 1992; Wang and Liebermann 1993). On the other hand, phase transition from cubic ($4/m\bar{3}2/m$) to rhombohedral ($32/m$) in LaAlO_3 , the rhombohedral twins with twin planes lying on both $\{110\}_r$ and $\{211\}_r$ were observed and their origin from losing the mirror plane symmetry $\{100\}_c$ and $\{110\}_c$, respectively, was suggested (Yao et al. 1992).

Transformation twins in LaGaO_3

LaGaO_3 is isostructural with the GdFeO_3 type ($Pnma$, $Z=4$) having a distorted perovskite structure due to tilting of the GaO_6 octahedra about three cubic $\langle 001 \rangle_c$ axes (Wang et al. 1991). The crystal structure of LaGaO_3 belongs to orthorhombic $Pnma$ with $a=0.54908$, $b=0.77725$, and $c=0.55227$ nm (Lerch et al. 2001) at ambient conditions. LaGaO_3 undergoes first-order transition (O'Bryan et al. 1990; Kobayashi et al. 1991; Wang et al. 1991; Yao et al. 1991) to rhombohedral $R\bar{3}c$ at 145°C . Both $Pnma$ and $Pbnm$ settings for the crystal axes have been commonly adopted in the literature as symbols for space group No. 62. $Pnma$, the standard setting of axes (Hahn 1987), is preferred here using the latest structural data of LaGaO_3 reported by Lerch et al. (2001), where the Ga atom is located at the origin instead of $(0.5, 0, 0)$ (Marti et al. 1994). This is also compatible with that used by the software package CaRIneTM Crystallography (version 3-1) for structure simulations.

Figure 1a, b show the orthorhombic and rhombohedral unit cells, both are plotted on the basis of the pseudo-cubic (pc) subcell ($a_c \approx b_c \approx c_c$). Some of the corresponding direction and plane indices between the orthorhombic and rhombohedral unit cell are listed in Table 1.

Transformation-induced twins in LaGaO_3 perovskite have been characterized before, but they were limited to using single crystals (Wang et al. 1991; Yao et al. 1991; Fink-Finowicki et al. 1992; Bdikin et al. 1993; Dudley

and Yao 1993). The twin operations in the low-temperature orthorhombic phase were found predominantly of the mirror reflections on $\{121\}$ and $\{101\}$ (adopting $Pnma$). The $\{121\}$ and $\{101\}$ twins determined for single-crystal LaGaO_3 cycled in situ through the phase transformation temperature (145°C) using optical microscopy (Fink-Finowicki et al. 1992), transmission electron microscopy (TEM) (Wang et al. 1991), and synchrotron X-ray topography (Yao et al. 1991; Bdikin et al. 1993; Dudley and Yao 1993) were generally consistent. Since o- LaGaO_3 is centrosymmetric, twins at room temperature are limited to only the reflection and rotation types (Bilby and Crocker 1965; Christian 2002). Twinning on $\{121\}$ was identified and determined as the reflection type, and the $\{121\}$ twin planes corresponding to the rhombohedral mirror plane $\{1\bar{1}0\}_r$ were derived using transformation matrices (Wang and Lu 2006). In addition to the orthorhombic twins lying on $\{121\}$ and $\{101\}$, in situ high-temperature TEM (Wang et al. 1991, 1992; Yao et al. 1991) has also revealed that the $\{110\}_r$ twins were the dominant feature of the high-temperature rhombohedral phase.

We have studied pressureless-sintered LaGaO_3 ceramics using TEM, aiming to resolve the phase-transformation domains induced by the $r \rightarrow o$ phase transition. The $\{101\}$ twins found in polycrystalline LaGaO_3 are identified as the reflection type by tilting techniques (Boulesteix et al. 1976; Manolikas et al. 1979) under TEM. How $\{101\}$ twins, and $\{121\}$ twins reported previously (Wang and Lu 2006), were generated and retained upon phase transition is discussed in terms of the transformation sequence $r \rightarrow c \rightarrow o$, with c being a metastable transition state (Christy 1993).

Table 1 Correspondences of directions and planes between cubic, rhombohedral, and orthorhombic unit cells

Cubic	Rhombohedral	Orthorhombic
Directions		
[100]	$\frac{1}{2}[11\bar{1}]$	$\frac{1}{2}[101]$
[010]	$\frac{1}{2}[\bar{1}11]$	$\frac{1}{2}[010]$
[001]	$\frac{1}{2}[1\bar{1}1]$	$\frac{1}{2}[\bar{1}01]$
[01 $\bar{1}$]	$[\bar{1}10]$	$\frac{1}{2}[11\bar{1}]$
[10 $\bar{1}$]	$[01\bar{1}]$	[100]
[1 $\bar{1}0$]	$[10\bar{1}]$	$\frac{1}{2}[1\bar{1}1]$
[011]	[001]	$\frac{1}{2}[\bar{1}11]$
[101]	[100]	[001]
[110]	[010]	$\frac{1}{2}[111]$
[111]	$\frac{1}{2}[111]$	$\frac{1}{2}[012]$
Planes		
(100)	(110)	(101)
(010)	(011)	(020)
(001)	(101)	(101)
(011)	(112)	(121)
(101)	(211)	(002)
(110)	(121)	(121)
(01 $\bar{1}$)	(1 $\bar{1}0$)	(121)
(10 $\bar{1}$)	(01 $\bar{1}$)	(200)
(1 $\bar{1}0$)	(10 $\bar{1}$)	(121)

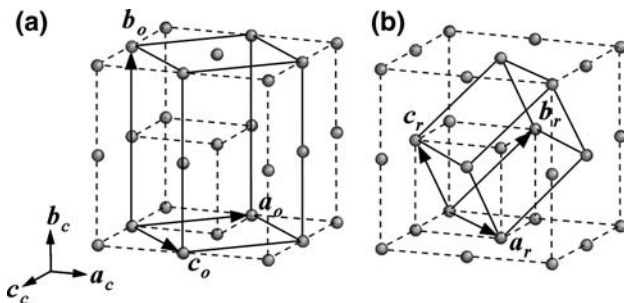


Fig. 1 Orthorhombic (a) and rhombohedral (b) unit cells of LaGaO_3 derived from the pseudo-cubic one

Experimental

A stoichiometric LaGaO_3 powder was prepared by reacting La_2O_3 (99.9% pure, Meldform Metals, Royston, UK) with Ga_2O_3 (99.9% pure, Meldform Metals) at 1:1 molar ratio in solid state by the mixed oxides technique. La_2O_3 , which can be easily hydrolyzed to form $\text{La}(\text{OH})_3$, was calcined at $1,000^\circ\text{C}$ for 2 h in air before weighing. It was then mixed with Ga_2O_3 in a ball mill with acetone using yttria-stabilized- ZrO_2 (YSZ) balls in a polyethylene (PE) 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 $150\text{ }\mu\text{m}$ -mesh, the powders were calcined at $1,000^\circ\text{C}$ for 4 h and de-agglomerated again before being pressed into discs of 10 mm diameter using a WC-inserted steel die at a uniaxial pressure of 35 MPa. The discs were sintered in air at $1,500^\circ\text{C}$ for 4 h at the heating and cooling rate of $5^\circ\text{C}/\text{min}$.

The microstructure was characterized using a JEOLTM AEM 3010 (Tokyo, Japan) operating at 300 kV. As-sintered discs (of $\sim 1200\text{ }\mu\text{m}$ thick) were ground on both sides to approximately half the thickness before being polished on one side using diamond lapping films (3 M, St Paul, MN, USA) successively to $\sim 1\text{ }\mu\text{m}$ surface roughness and $\sim 300\text{ }\mu\text{m}$ thickness. After being mounted on a glass slide and using a home-made tripod polisher, the unpolished side was further polished down to similar surface roughness to thin sections of $< 20\text{ }\mu\text{m}$ thickness. Thin sections were carefully cut and stuck onto 3 mm (ϕ) Cu-rings using G1 glue (Gatan, Pleasanton, CA, USA) before Ar ion beam thinned to electron transparency using a Gatan ion-miller (Duo-MillTM or PIPSTM).

Results

The LaGaO_3 samples used in this study had been characterized (Wang and Lu 2006) for phase contents and domain structures before. They contained predominantly o- LaGaO_3 together with minor amounts of both second phase $\text{La}_4\text{Ga}_2\text{O}_9$ and unreacted Ga_2O_3 . Sintered samples exhibited a variety of domain configurations where lamellar twin domains were ubiquitous. Three types of twins lying on $\{121\}$, $\{123\}$, and rotating about $[010]_{90^\circ}$ were identified, and their crystallography has been analysed and reported.

Additionally, the $\{101\}$ twins have been identified in this study. Its characteristic crystallographic orientation relationships distinguished them from other transformation twins of the orthorhombic perovskites (Wang and Lu 2006). In order that the zone axes across domain boundaries were differentiated unequivocally, corresponding diffraction patterns have been analysed and determined for the twin relationships.

Diffraction patterns for orthorhombic LaGaO_3

Selected area diffraction patterns (SADPs) from o- LaGaO_3 grains were indexed according to the space group $Pnma$, and with the orthorhombic unit cell of $a_o \times b_o \times c_o$ shown in Fig. 1a. Since the orthorhombic cell is based on the unit cell of the cubic aristotype perovskite, $a_o \approx [101]_c$, $b_o \approx 2b_c$, $c_o \approx [101]_c$, the lattice parameters $a_o \approx c_o \approx (1/\sqrt{2})b_o$, resulting in clusters of almost identical d -spacings and indistinguishable $\{hkl\}$ reflections in reciprocal space, e.g., $d_{100} \approx d_{001}$, $d_{110} \approx d_{011}$, $d_{020} \approx d_{101}$, and $d_{200} \approx d_{002} \approx d_{121}$. Therefore, indexing such patterns is not always unambiguous, as seen with other orthorhombic perovskites such as CaTiO_3 and MgSiO_3 (Hu et al. 1992; Wang et al. 1990, 1992; Wang and Liebermann 1993). Although the occurrence of double diffractions has facilitated the identification of g -vectors 020 and 101 from $Z=[101]$ (Wang and Lu 2006), similar ambiguities still arise with assigning the zone axis uniquely for other zone patterns. For example, the SADP of $Z=[100]$ is almost identical (Hu et al. 1992) to that of $Z=[111]$ with $d_{020} \approx d_{101}$ and $d_{002} \approx d_{121}$. As a result, they cannot be differentiated by the conventional procedures of indexing diffraction patterns. Other approaches were sought and described below.

Figure 2 shows how the SADP of $Z=[110]$ can be distinguished from that of $Z=[011]$. They have almost identical d -values and were not differentiable from measurements on the patterns, e.g., reciprocal lattices 200 or 002, and 110 or 011. However, it was found that not only the reflections of $(1\bar{1}1)$ and $(11\bar{1})$, as arrowed correspondingly in Fig. 2a, b, differed significantly in intensities, but also they arrived at two different zones of $Z=[100]$ and $[001]$, respectively, when tilted further along the $002^* - 00\bar{2}^*$ and $200^* - \bar{2}00^*$ pairs of Kikuchi

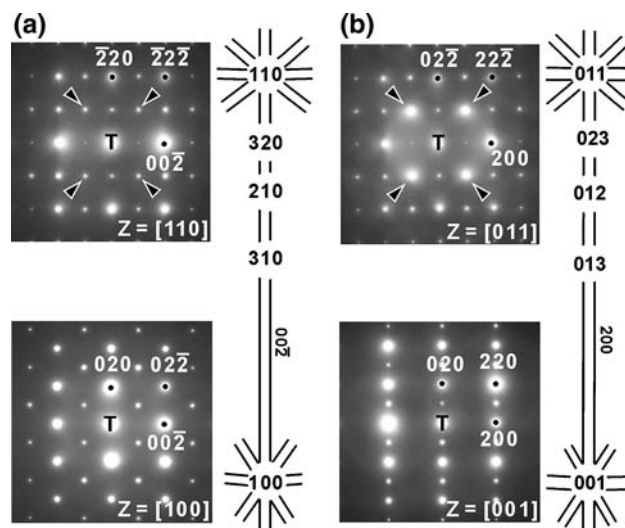


Fig. 2 Differentiation between $Z=[110]$ and $Z=[011]$ using tilting the foil to **a** $Z=[100]$ and **b** $Z=[001]$, respectively (TEM). Arrows indicate the diffraction characteristics significantly different in intensities

lines. Consequently, both spot intensities and further zone tilting made unambiguous discrimination between them. Therefore, differentiating the zone axis $[110]$ from $[011]$ was readily accomplished by tilting the foil to the next available low index zones along the $002^* - 00\bar{2}^*$ or $200^* - 200^*$ pairs of Kikuchi lines.

$\{101\}$ Twinning—viewing from $[0\bar{1}0]_A$ and $[010]_B$

One of the grains in LaGaO_3 ceramics containing multiple twin domains is shown in Fig. 3i. Separated by domain boundaries, the domains are designated A, B, C, D, E, F, G, and H, correspondingly, as indicated.

The foil has been tilted such that domain A appeared in the exact zone axis of $Z_A = [0\bar{1}0]$ and imaged in bright field (BF). The diffraction aperture was then shifted successively to each of the other domains and SADP for each domain was recorded accordingly. The SADPs of domains A to H are given in Fig. 3a to h, respectively. Figure 3a is indexed to orthorhombic $Z_A = [0\bar{1}0]$. According to Hahn (1987), the sets of reflection on $(h00)$ with $h=2n$; $(00l)$ with $l=2n$; (hkl) with $h+l, k=2n$ are allowed reflections of $Pnma$. The forbidden reflections, i.e., (100) and (001) , indicated by arrows in the SADP from $Z_A = [0\bar{1}0]$, have emerged due to double diffraction (Hu et al. 1992). The SADP of domain B (Fig. 3b) indexed to $Z_B = [010]$ was almost identical to that of domain A, only that the systematic rows of reflections (100) and (001) have interchanged between zones Z_A and Z_B . In fact, 100^* and 001^* cannot be differentiated

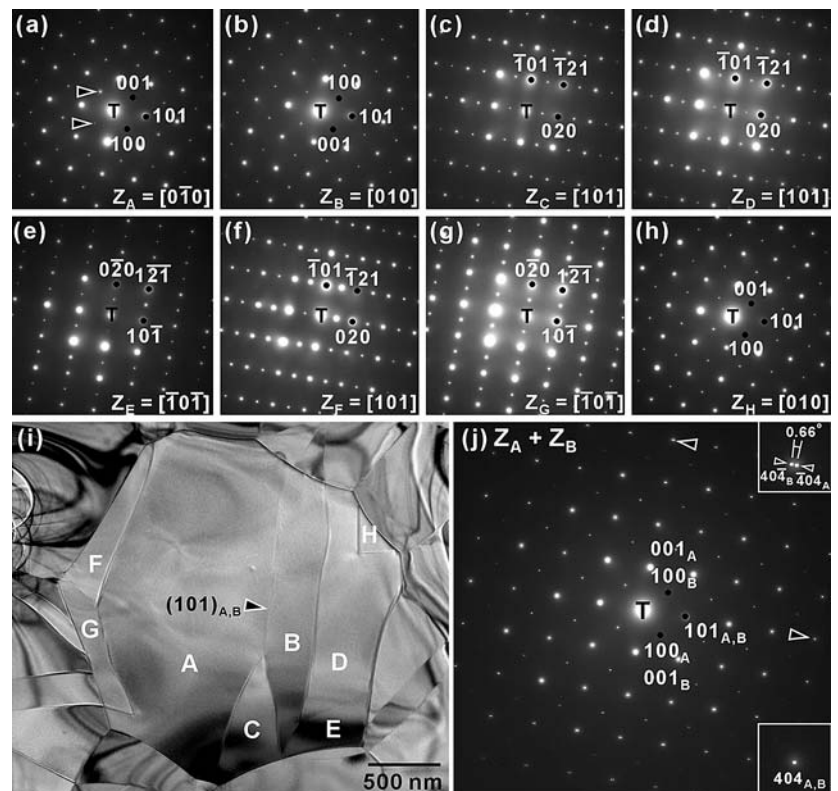
directly from measuring the d -values since $a_o \approx c_o$. They could only be determined experimentally by tilting the foil to $Z=[110]$ or $[011]$.

The SADP taken across domain boundary A–B with electron beam parallel to the boundary plane is shown in Fig. 3j. The boundary of domains A and B exhibited no fringe contrast implying that it was lying parallel to the electron beam and imaged in edge-on conditions.

Only one unsplit row of reflections (USR) (Boulesteix et al. 1976; Manolikas et al. 1979) along the reciprocal direction $(101)^*_{A,B}$ contributed from both domains A and B was discerned in the direction perpendicular to the twin boundary. The existence of USR along 101^* was confirmed from high-order reflections along the $(101)^*$ reciprocal direction. The (404) reflection, indicated and shown in the inset in Fig. 3j, appeared as one coincident spot was in fact contributed simultaneously by the $(404)_A$ and $(404)_B$ reflections from twinned crystal parts A and B, respectively. Accordingly, the A–B twin boundary being plane (101) (as indicated), common to domains A and B, can be determined readily.

Although the diffraction pattern of domain A was almost identical to that of domain B, spot splitting caused by a slight discrepancy in the g vectors simultaneously reflecting from two crystal parts was detected in the SADP containing both domains (shown in Fig. 3j). This was only discerned with significant reduction of the exposure time by two-third (Wang and Lu 2006), as shown inset in Fig. 3j. Examining high-order reflections along the $(\bar{1}01)^*_A$ direction, e.g., (404) of domain A and (404) of domain B, as indicated in Fig. 3j, spot splitting

Fig. 3 TEM bright-field (BF) image, showing a LaGaO_3 grain (i) containing multiple twin domains designated from A to H, (a) to (h) corresponding SADPs, and (j) SADP from both domains A and B



from $(\bar{4}04)_A$ to $(40\bar{4})_B$ by an angle $2\phi \approx 0.66^\circ$ [where ϕ is the obliquity (Cahn 1954)] of counterclockwise rotation along $(\bar{1}01)_A$ about $Z_A = [0\bar{1}0]$ was recognized. The spot splitting appeared in a direction parallel to 101^* USR; in other words, it was perpendicular to the (101) twin plane. Other spots were also split in the direction parallel to 101^* USR and by an amount proportional to their distance from the 101^* USR. These characteristics suggest (Boulesteix et al. 1976; Manolikas et al. 1979) that twinning on (101) is the reflection type.

Zones from domains A, B, and C are in parallel, i.e., $[0\bar{1}0]_A // [010]_B // [101]_C$, when one (A–B) of the three twin boundaries was viewed in edge-on conditions (Fig. 3i). Twin boundary A–B lying in the $(101)_{A,B}$ plane (as indicated) was then determined directly from corresponding SADPs shown in Fig. 3a, b. Spot splitting detected from the $\{101\}$ twins was larger than that observed in the $\{121\}$ twins ($\sim 0.22^\circ$) by three times (Wang and Lu 2006). The spot splitting of domains A and B is twice of the obliquity (ϕ), which is calculated by the following equation (Wang et al. 1992),

$$\phi = 2 \tan^{-1}(c/a) - 90 \text{ deg} \quad (1)$$

where a and c are the lattice parameters of the orthorhombic cell (Lerch et al. 2001).

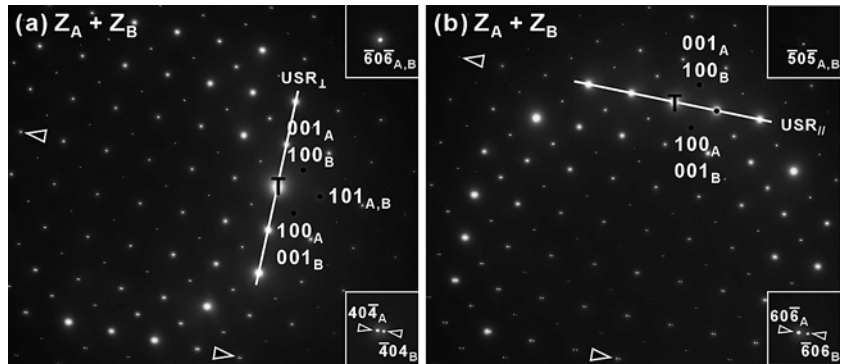
The $\{101\}$ twins in LaGaO_3 were also confirmed to be a reflection twin by exploring the reciprocal lattices. A tilting experiment in the microscope (Boulesteix et al. 1976; Manolikas et al. 1979) was adopted to differentiate reflection twins from rotation ones. Figure 4a, b show the SADP of the A–B domain boundary with the foil tilted away from the exact zone axis. Consequently, the SADP of the two crystal parts was tilted clockwise about the direction perpendicular to the 101^* USR (denoted $\text{USR}_\perp$ in Fig. 4a). In contrast to the SADP obtained while the twin boundary was viewed edge-on (shown in Fig. 3j), here the twin plane (101) has become slightly inclined to the electron beam. Examining high-order reflections along 101^* USR, e.g., $(\bar{6}0\bar{6})$ of domain A and $(\bar{6}0\bar{6})$ of domain B, as indicated and shown in the inset in Fig. 4a, only one coincident spot appeared in the reciprocal lattice, which suggests the (101) plane is common to adjacent domains. Spot splitting appeared in

other rows, e.g., $(40\bar{4})_A$ and $(\bar{4}04)_B$, as indicated and shown in the inset in Fig. 4a, where the direction of splitting was still parallel to 101^* USR and the magnitude of splitting increased with the distance to the USR. Similarly, Fig. 4b shows the SADP obtained by tilting the crystal clockwise about the direction parallel to the USR (denoted $\text{USR}_\parallel$ in Fig. 4b). The (101) twin boundary remained edge-on and was parallel to electron beam. Again, the reflections appeared in the high order along $(101)^*_{A,B}$ were still coincident and the other rows were split in the same direction parallel to the 101^* USR, as shown in the inset in Fig. 4b. Therefore, the $\{101\}$ twins are the reflection type whose corresponding SADP contains only one row of unsplit spots and the spot splitting remains parallel to the USR (Boulesteix et al. 1976; Manolikas et al. 1979).

The dynamic contrast of 101 domain walls inclining to the electron beam was in accordance with the characteristics of δ -fringes (Amelinckx et al. 1978, 1984). The (101) twin boundary has been imaged in both BF (Fig. 5a) and dark field (DF) (Fig. 5b) using $g = 002$ of domain A, and for clarity the framed regions at a higher magnification are also shown inset. The extreme fringes were therefore consistent with the nature of the δ -type where they are asymmetric about the centre in BF image (i.e., bright-dark, BD, shown in Fig. 5a) and symmetric in DF image (i.e., bright-bright, BB or dark-dark, DD, shown in Fig. 5b). The black dots segregated along domain boundaries, as indicated in Fig. 5a, are dislocation loops generated by irradiation damage under 300 keV electron beam.

The displacement vector ($\mathbf{R}$) across the (101) twin interface was also determined by adopting the invisibility criteria $2\pi\mathbf{g}\cdot\mathbf{R} = 0$ or $2n\pi$, where n =integer (Amelinckx et al. 1978). It is found accordingly that the fault vector $\mathbf{R} = \varepsilon[10\bar{1}]$ has a non-fractional displacement, where ε is the irrational length. Similar to those determined for the ferroelectric domain boundaries in tetragonal BaTiO_3 (Chou et al. 2000), the vectors have their length (ε) non-fractional and not related to the unit lattice translation vector in a simple way (Malis and Gleiter 1976). The fault vector is therefore lying in (and parallel to) the twin plane.

Fig. 4 Tilting experiment showing the corresponding SADP that is **a** perpendicular to USR ($\text{USR}_\perp$) and **b** parallel to USR ($\text{USR}_\parallel$) (TEM)



Crystallographic orientation relationships of {101} twinning

The crystallographic orientation relationships for twinning on {101} are illustrated in Fig. 6 for two crystal parts by corresponding SADPs. Similarly, these SADPs were recorded by tilting the foil to an exact zone axis for domains A, the diffraction aperture was then shifted to the other twin domain B to obtain its corresponding diffraction patterns.

Finding and starting from $Z_A = [0\bar{1}0]$, the crystal was tilted along the pairs of Kikuchi lines of either 200^* or 002^* ; then the $\bar{1}01^*$ pair to arrive at other zone axes en route (referred to Fig. 6). Diffraction patterns of four common low-index zone axes thus obtained from domain A are shown in Fig. 6a2 to a5, and corresponding SADPs of domain B in Fig. 6b2 to b5, respectively. Observing the SADPs, it was found that the patterns

obtained from domain A were in close resemblance to those of domain B. Owing to similar lattice parameters $a_o \approx c_o$ of the orthorhombic cell (Lerch et al. 2001), indexing of these diffraction patterns again became ambiguous.

Zone axes $[1\bar{1}0]$ and $[011]$ may again be determined unequivocally by tilting the crystal to $[100]$ or $[001]$, as described previously. The SADP of zone axis $[011]$ exhibited some characteristic features such as reflection spots with stronger intensities and spot streaking (referred to Fig. 6b3) in contrast to that of zone axis $[1\bar{1}0]$. These peculiarities are easily observed by comparing the diffraction patterns in Fig. 6a3, b3. Accordingly, the SADP of domain B was assigned to zone of the $[011]$ type because the intensity of reflection spots appeared at the $\bar{1}1\bar{1}^*$ set was stronger than that of the same set from domain A (also referred to Fig. 2a, b). A discrepancy in the intensities of reflection spots is so significant that

Fig. 5 **a** BF and **b** DF images of the inclined twin boundary (101), showing the characteristics of δ -fringes. The extreme fringes are asymmetric in BF [indicated by B (*bright*) and D (*dark*)] and symmetric in DF (indicated by D and D) (TEM). Unfilled arrow indicates dislocation loops

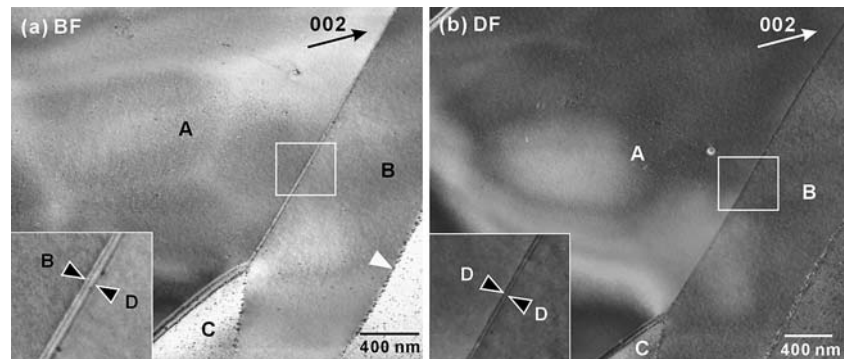
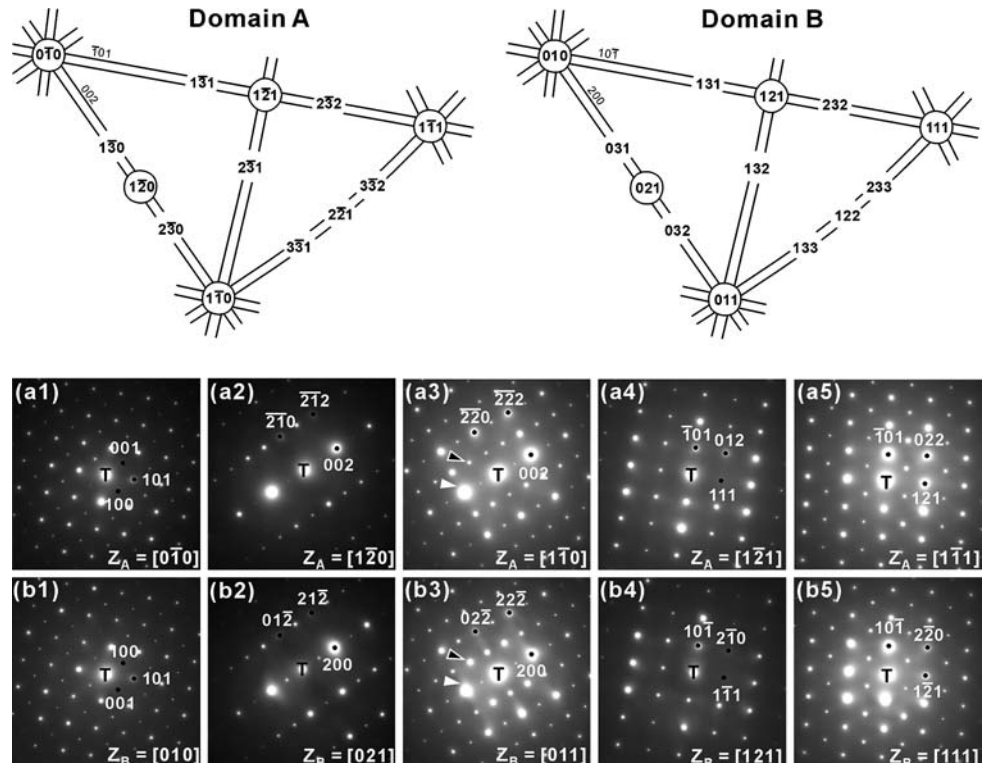


Fig. 6 Crystallographic orientation relationships for twinning on $(101)_{A,B}$; **a** the SADPs of domain A, and **b** corresponding SADPs of domain B (TEM)



$\bar{1}\bar{1}\bar{1}^*$ (of $Z_A = [\bar{1}\bar{1}0]$) and $\bar{1}\bar{1}\bar{1}^*$ (of $Z_B = [011]$) can be readily differentiated, as indicated by filled arrows in Fig. 6a3, b3.

Furthermore, spot streaking observed at the $200^* - \bar{2}00^*$ pair of reflections, as indicated by unfilled arrows in Fig. 6b3, has enabled us to determine the zone axis in domain B to $Z_B = [011]$. Likewise, that in domain A (Fig. 6a3) is assigned to $Z_A = [\bar{1}\bar{1}0]$. Other zone axes were accordingly determined for domains A, i.e., $[0\bar{1}0]$, $[1\bar{2}0]$, $[\bar{1}\bar{2}1]$, and $[\bar{1}\bar{1}1]$ while corresponding zone axes of domain B became $[010]$, $[021]$, $[121]$, and $[111]$, as shown in Fig. 6.

It is of importance to realize that for the $(101)_{A,B}$ twins the 200 and 002 reflections in domains A and B, respectively, are interchanged with each other (Wang et al. 1990; Fink-Finowicki et al. 1992) as the crystal moves from one domain (domain A) to the adjacent one (domain B), or vice versa. Exploring the diffraction patterns in Fig. 6a1, b1, it can also be deduced that the b -axis (long axis in $Pnma$) has rotated by 180° across the (101) twin boundary of domains A and B.

Discussion

Intermediate metastable structure

The traditional Ehrenfest classification divides phase transitions into ‘first order’ and ‘second order’ types. First-order transitions initiate by discrete nucleation events and show discontinuities in first derivatives of free energy (volume, entropy). Second-order transitions show discontinuities only in second derivatives of free energy (compressibility, heat capacity, expansivity) and may occur without loss of structural coherence between the two phases. Landau theory (Tolédano and Tolédano 1987) requires that strict symmetry relationships are satisfied for second-order character to be possible. The symmetry of one structure should be a subgroup of that of the other, the degree of symmetry breaking being quantified by an order parameter Q . The free energy difference between structures must then be an even function of Q . The order parameter must transform as the identity representation of the lower symmetry, and as non-identity irreducible representation corresponding to a possible distortion mode of the higher symmetry.

Loss of structural coherence between phases implies that first-order transitions would not be expected to show twinning relationships between differently oriented domains of low-symmetry structure, since twins originate in the multiple ways in which the symmetry of the parent high-symmetry structure can be broken. However, Christy (1993) demonstrated that transitions which do not satisfy the Landau criterion for continuity may nevertheless be continuous and diffusionless if they can occur *via* second-order transition to and from a metastable transition state that is of subgroup or supergroup symmetry common to the two end phases (‘Type II’), or

via a chain of such transitions (‘Type III’). In such cases, orientation relationships are preserved and systematic twin relationships may give an indication of the exact mechanism.

Interconversions between some of the perovskite tilt systems of Glazer (1975) were evaluated for first- or second-order character by Aleksandrov (1976) and Howard and Stokes (1998). The transition from $R3c$ (Glazer notation $a^-a^-a^-$) to $Pnma$ ($a^-b^+a^-$) cannot be second order, but is commonly observed in perovskites with rare-earth elements in the A-site, e.g., LaGaO_3 (Wang et al. 1991), LaMnO_3 (Arao et al. 2000), LaCrO_3 (Hashimoto et al. 2000), and PrNiO_3 (Huang et al. 1990). The orthorhombic and rhombohedral symmetries do not show a group-subgroup relationship, so the transition between them must be first order (O’Byrne et al. 1990). Type II diffusionless martensitic transitions might nevertheless be possible via an intermediate structure which is either a highest common subgroup symmetry [i.e., $P2_1/c$ (No.14)] or a lowest common supergroup symmetry [i.e., $Pm\bar{3}m$ (No.221)] of $R3c$ and $Pnma$ (Bloss 1971; Stokes and Hatch 1988). Indeed, regarding the *aristotype* $Pm\bar{3}m$ as an intermediate (Arao et al. 2000), twin domains of $\{110\}$ and $\{112\}$ (of $Pbnm$) induced upon the $r \rightarrow c_{(i)} \rightarrow o$ transition (where subscript i for intermediate) in $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ have been identified by TEM.

The crystallographic origin of transformation-induced twins lying on $\{101\}$ and $\{121\}$ is discussed from loss or gain of symmetry elements (Guymont 1981; Nord 1992, 1997) upon the $r \rightarrow o$ transition via an intermediate phase of cubic $Pm\bar{3}m$, i.e., rhombohedral $\rightarrow$ cubic_(i) $\rightarrow$ orthorhombic. Table 2 lists the relevant crystallographic data of the three polymorphs of LaGaO_3 . The twin laws thus derived are consistent with experimental observations.

Orientation variants of $\{101\}$ and $\{121\}$ twins

Polycrystalline LaGaO_3 grains often exhibit multiple twin domains with several representative configurations. Some domains were lamellar in shape with boundaries parallel to one another, some having their boundaries converged to a triple junction (e.g., A–B–C in Fig. 3i) exhibited three orientation variants. This type of domain configuration is commonly observed from sintered LaGaO_3 (Wang and Lu 2006), including domains A–B–C, A–F–G, and B–D–E shown in Fig. 3i.

Change in point group symmetry upon phase transition from high to low symmetry phase constitutes the twin laws. The twin relations can be evaluated by investigating loss or gain of symmetry elements through the transition (Guymont 1981; Nord 1992, 1997). Table 2 lists the relevant crystallographic data of the rhombohedral, cubic and orthorhombic phases of LaGaO_3 . Twins induced by symmetry change upon phase transition from $r \rightarrow c_{(i)} \rightarrow o$ are indicated.

Table 2 Point group symmetry elements loss sequentially from rhombohedral to cubic intermediate phase, and to orthorhombic with relevant transformation-induced twins

Rhombohedral ($\bar{3}2/m$) $\rightarrow$		Cubic ($4/m\bar{3}2/m$) $\rightarrow$		Orthorhombic ($2/m2/m2/m$)
$\bar{3}$	$[111]_r$	$\bar{3}$	$\langle 111 \rangle_c$	Three orientation variants (along $\langle 210 \rangle$ or $\langle 012 \rangle$)
$2/m$	$[\bar{1}\bar{1}0]_r / (\bar{1}\bar{1}0)_r$ $[01\bar{1}]_r / (01\bar{1})_r$ $[10\bar{1}]_r / (10\bar{1})_r$	$2/m$	$[01\bar{1}]_c / (01\bar{1})_c$ $[10\bar{1}]_c / (10\bar{1})_c$ $[\bar{1}\bar{1}0]_c / (\bar{1}\bar{1}0)_c$	$\{121\}$ twins (loss of m) $\{123\}$ twins (loss of 2)
		Gain	$[011]_c / (011)_c$	
		$2/m$	$[101]_c / (101)_c$	
			$[\bar{1}10]_c / (\bar{1}10)_c$	
		Gain	$[100]_c / (100)_c$	$\{101\}$ twins (loss of m)
		$4/m$	$[010]_c / (010)_c$	$[010]_{90^\circ}$ twins (loss of 4)
			$[001]_c / (001)_c$	

Three orientation variants found in Fig. 3i are derived from loss of the threefold rotation axis ($\bar{3}$ in point group $4/m\bar{3}2/m$ of cubic_(i) $Pm\bar{3}m$) when arrives at orthorhombic $Pnma$ (point group $2/m2/m2/m$) upon the $c_{(i)} \rightarrow o$ transition (Arao et al. 2000; Wang and Lu 2006). Loss of the threefold rotation axis should have produced the $\{121\}_{120^\circ}$ rotation twins with an angle of 120° between two adjacent twin boundaries about the twin axis $\langle 210 \rangle$ or $\langle 012 \rangle$ (corresponding to $[111]_r$ and $\langle 111 \rangle_c$; Table 2) in the orthorhombic phase. Such domain configurations have not been observed in the present samples, nor reported before in the literature. Nevertheless, consistent with Table 2, the $[010]_{90^\circ}$ rotation twins from loss of fourfold rotation axis were identified before in sintered o-LaGaO₃. Because the fourfold rotation axis does not exist in the rhombohedral phase, the twins could only be derived from loss of the fourfold rotation axis upon transformation from the cubic symmetry (loss of 4 in Table 2). While the reflection twins are induced by loss of mirror symmetry, the lost threefold rotation axis retained in o-LaGaO₃ has produced orthorhombic variants. Consequently, each of the reflection twins contains three orientation variants and with twin planes lying on $\{101\}$ (Fig. 3), $\{121\}$ (Wang and Lu 2006), and $\{123\}$ (unpublished data). The former two types have been confirmed here experimentally as shown in Fig. 3i with corresponding SADPs.

The fact that twins on $\{121\}$ appeared in three orientation variants is due to the three possible orientations for the orthorhombic b -axis (Fink-Finowicki et al. 1992; Arao et al. 2000; Wang and Lu 2006). Such transition via a shear deformation mechanism was suggested by Arao et al. (2000) when the rotational displacement of MnO₆ octahedra changed from the R_{25} phonon mode to M_3 along the z -axis with three choices of rotation axis. Three $\{121\}$ domains converged to a triple junction necessitates one of the three variants be viewed from $\langle 010 \rangle$ and the other two from $\langle 101 \rangle$. Additionally, the crystallographic directions of the three orientation variants should be parallel to one another, i.e., $\langle 010 \rangle // \langle 101 \rangle // \langle \bar{1}0\bar{1} \rangle$ amongst any three domains in sintered LaGaO₃, e.g., $\langle 010 \rangle_A // \langle 101 \rangle_F // \langle \bar{1}0\bar{1} \rangle_G$ for domains A–F–G and $\langle 010 \rangle_B // \langle 101 \rangle_D // \langle \bar{1}0\bar{1} \rangle_E$ for domains B–D–E (referred to Fig. 3). Here, the reason

why the orientation relationship $[0\bar{1}0]_A // [010]_B // [101]_C$ was observed in domains A–B–C, instead of the common $\langle 010 \rangle // \langle 101 \rangle // \langle \bar{1}0\bar{1} \rangle$, is that the twin lying in $(101)_{A,B}$ was detected (Fig. 3). Therefore, with identical zone relationships for domains B and C, i.e., $[010]_B // [101]_C$, and domains A and C, i.e., $[0\bar{1}0]_A // [101]_C$, the domain boundaries would lie in $\{121\}$. Consistent with other perovskites (e.g., CaTiO₃ and MgSiO₃), twinning on $\{101\}$ is not as frequently observed as that on $\{121\}$.

Two orientation variants sharing twin boundary (101) are therefore transformation-induced domains A and B, where the obliquity $\phi \approx 0.33^\circ$ (shown inset in Fig. 3j) can be differentiated from the corresponding SADP of $Z_A + Z_B$ (Fig. 3j). Since orthorhombic $Pnma$ is centrosymmetric retaining the inversion centre, twins are limited to the reflection and rotation types from high- to low-symmetry phase transition. The $(101)_{A,B}$ twin is indeed of the reflection type, as confirmed by tilting experiments (Fig. 4), and domains A and B are therefore related by a reflection operation crystallographically (i.e., loss of m , Table 2), as illustrated schematically in Fig. 7. However, change of Bravais lattice from rR to oP also induces anti-phase boundary (APB) domains (Arao et al. 2000) which have been identified in o-LaGaO₃.

Analysing the microstructure in orthorhombic LaGaO₃, both transformation-induced $\{101\}$ and $\{121\}$ twins were found in grains containing multiple domains. Both twins are of the reflection type. Their crystallography is consistent with the twins derived by considering

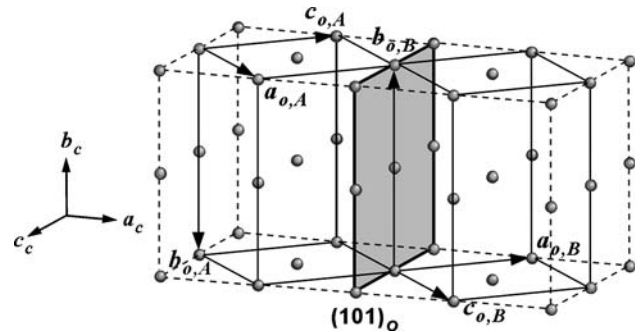


Fig. 7 Schematic illustration of domains A and B related by a (101) reflection operation

an intermediate metastable structure (cubic $Pm\bar{3}m$ of the lowest common supergroup symmetry) between rhombohedral and orthorhombic following the transition sequence of rhombohedral $\rightarrow$ cubic_(i) $\rightarrow$ orthorhombic.

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