Supplementary information

Orientation domains in the intermediate product Na_3TiOF_5 during the synthesis of anatase TiO_2 nanosheets with exposed reactive {001} facets

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According to Hermann's theorem, the subgroup H of the space group G is general (*allgemein*) if H is neither k subgroup (*klassengleiche* subgroup) nor t subgroup (*translationengleiche* subgroup) (Wondratschek, 2004; Wondratschek & Jeitschko, 1976; Wang & Kuo, 1990). In other words, H has lost both translational operations and crystal class operations. Hermann's theorem mentions that for each subgroup H of the space group G there is a intermediate space group M which is the maximal t subgroup of G and also the minimal k supergroup of H (Hermann, 1929). Based on analyzing the group-subgroup relations, we got the intermediate space group $C2/m$, and the maximal subgroup chain from $Fm\bar{3}m$ to $P2_1/n$ can be determined as following:

$$Fm\bar{3}m \supset [t3]F4/m12/m(I4/mmm) \supset$$
$$[t2]I2/m2/m1(Immm) \supset [t2]I12/m1(C2/m)$$
$$\supset [k2]P12_1/a1(P2_1/n) \tag{s1}$$

The contents in the square brackets represent the type (*klassengleiche* or *translationengleiche*) and the order of each subgroup *H* in its supergroup *G*. Then the Hermann-Mauguin symbol of *H* which is in the same coordinate system with *G* are shown. The contents in the round brackets denote the conventional short Hermann-Mauguin symbol.

The corresponding left coset decomposition of the supergroup $Fm\bar{3}m$ with respect to the intermediate space group and the coset relation of the intermediate group $C2/m$ and its subgroup in the equation (s1) are expressed as:

$$Fm\bar{3}m = \{I \oplus 3^+[111]_c \oplus 3^+[1\bar{1}\bar{1}]_c \oplus 3^+[\bar{1}1\bar{1}]_c$$
$$\oplus 3^+[\bar{1}\bar{1}1]_c \oplus 3^-[111]_c \oplus 3^-[1\bar{1}\bar{1}]_c \oplus 3^-[\bar{1}1\bar{1}]_c \tag{s2}$$
$$\oplus 3^-[\bar{1}\bar{1}1]_c \oplus 2[001]_c \oplus 2[010]_c \oplus 2[100]_c\}C2/m$$

$$C2/m = \{I \oplus t(0,1/2,1/2)_m\}P2_1/n \tag{s3}$$

where *I* is the identity operation while $\oplus$ represents the addition of two symmetry operations. $3^+[111]_c$ and $3^-[111]_c$ (the subscript "c" denotes the pseudo-cubic cell) denote the +2π/3 and -2π/3 rotations both around the $[111]_c$ direction. $2[001]_c$ denotes the twofold axis along $[001]_c$ direction. $t(0,1/2,1/2)_m$ is a translation operation in the monoclinic cell with space group $C2/m$. It transforms to $t(-1/4,1/4,1/2)_c$ which is a translation operation with respect to the basic vectors of pseudo-cubic cell. The equation (s2) describes the *t* subgroup relation which means that the translation operations are preserved and the point symmetry is lost. Meanwhile, equation (s3) represents *k* subgroup relation in which the translation operations are lost. Relying on the analysis above, the left coset decomposition of the space group $Fm\bar{3}m$ with respect to its subgroup $P2_1/n$ is shown as following:

$$
\begin{aligned}
Fm\bar{3}m = \{ & I \oplus 3^{+}[111]_c \oplus 3^{+}[1\bar{1}\bar{1}]_c \oplus 3^{+}[\bar{1}1\bar{1}]_c \\
& \oplus 3^{+}[\bar{1}\bar{1}1]_c \oplus 3^{-}[111]_c \oplus 3^{-}[1\bar{1}\bar{1}]_c \oplus 3^{-}[\bar{1}1\bar{1}]_c \\
& \oplus 3^{-}[\bar{1}\bar{1}1]_c \oplus 2[001]_c \oplus 2[010]_c \oplus 2[100]_c \} \\
& P2_1/n \oplus \{ I \oplus 3^{+}[111]_c \oplus 3^{+}[1\bar{1}\bar{1}]_c \oplus 3^{+}[\bar{1}1\bar{1}]_c \\
& \oplus 3^{+}[\bar{1}\bar{1}1]_c \oplus 3^{-}[111]_c \oplus 3^{-}[1\bar{1}\bar{1}]_c \oplus 3^{-}[\bar{1}1\bar{1}]_c \\
& \oplus 3^{-}[\bar{1}\bar{1}1]_c \oplus 2[001]_c \oplus 2[010]_c \oplus 2[100]_c \} \\
& \mathrm{t}(-1/4,1/4,1/2)_c P2_1/n
\end{aligned} \tag{s4}
$$

Here we consider the domain with space group $P2_1/n$ as a reference. Thus, three types of domains are classified: one is *orientation domains* (*twin domains*) if variants transform into each other via the point group symmetry operations which don't belong to the space group of their common derived phase ($P2_1/n$ in this case), such as $3^{+}[111]_c P2_1/n$; the second one is *translation domains* (*antiphase domains*) which result from the loss of translational operations of the parent phase that don't belong to the space group of the derived phase, such as $\mathrm{t}(-1/4,1/4,1/2)_c P2_1/n$; the third kind of domains can be described as *translation twins* which transform into each other by combining the point group symmetry operations and the translation operations, such as $3^{+}[111]_c \mathrm{t}(-1/4,1/4,1/2)_c P2_1/n$. According to the experiment results, only the situation of *orientation domains* is considered. Then the *orientation domains* part in the equation (s4) is retained as following:

$$
\begin{aligned}
R = \{ & I \oplus 3^{+}[111]_c \oplus 3^{+}[1\bar{1}\bar{1}]_c \oplus 3^{+}[\bar{1}1\bar{1}]_c \oplus \\
& 3^{+}[\bar{1}\bar{1}1]_c \oplus 3^{-}[111]_c \oplus 3^{-}[1\bar{1}\bar{1}]_c \oplus 3^{-}[\bar{1}1\bar{1}]_c \\
& \oplus 3^{-}[\bar{1}\bar{1}1]_c \oplus 2[001]_c \oplus 2[010]_c \oplus 2[100]_c \} \\
& P2_1/n
\end{aligned} \tag{s5}
$$

The twelve cosets in the equation (s5) correspond to twelve orientation domain variants for the monoclinic phase.

Table S1 lists the orientation domain variants type D_i (here D_i denote monoclinic phase with space group $P2_1/n$, i ranges from 1 to 12) and the corresponding symmetry operations in left coset for these twelve variants. D_1 is considered as a reference domain variant. The geometric relation between domains and parent pseudo-cubic phase can be deduced mathematically from Table S1. The basic vectors $\mathbf{a}_i$, $\mathbf{b}_i$, and $\mathbf{c}_i$ of the monoclinic variant D_i can be related to those of $\mathbf{a}_c$, $\mathbf{b}_c$, and $\mathbf{c}_c$ of the pseudo-cubic crystal cell by

$$\mathbf{a_i} \quad \mathbf{b_i} \quad \mathbf{c_i} = \mathbf{a_c} \quad \mathbf{b_c} \quad \mathbf{c_c} \; M_i \tag{s6}$$

where M_i is the transformation matrix of the variant D_i. Table S2 lists all the matrices. These results facilitate our understanding of crystallographic relationships among different domain variants.

In current case, 11 types of domain boundaries are acquired and boundary between variant D_1 and D_j are represented by $I_{D1/Dj}$ (j ranges from 2 to 12). The necessary and sufficient conditions of the equivalence between domain boundaries $I_{D1/Dm}$ and $I_{D1/Dn}$ (both m and n range from 2 to 12, $m \neq n$) is either (1) there is a symmetry operation h which belongs to the subgroup H (in our case, $H = P2_1/n$) that can transform domain variant D_m to D_n or (2) for a symmetry operation h in the coset of domain variant D_m there is an inverse symmetry operation h^{-1} in the coset of domain variant D_n. Based on these rules, the equivalent relations of domain variants are listed in Table S3. Here, I, $2[\bar{1}10]$, $m[\bar{1}10]$ and $\bar{1}$ are operations of $P2_1/n$ which transform domains in column one to the domains in another column under the corresponding symmetry operation.

Based on equation (s6) and the transformation matrices in Table S2, the crystallographic orientation relationship between the pseudo-cubic parent phase and the monoclinic derived phase could be obtained by applying equations (s7) and (s8).

$$\mathrm{h_m} \quad \mathrm{k_m} \quad \mathrm{l_m} = \mathrm{h_c} \quad \mathrm{k_c} \quad \mathrm{l_c} \; M_i \tag{s7}$$

$$\begin{pmatrix} \mathrm{u_m} \\ \mathrm{v_m} \\ \mathrm{w_m} \end{pmatrix} = (M_i)^{-1} \begin{pmatrix} \mathrm{u_c} \\ \mathrm{v_c} \\ \mathrm{w_c} \end{pmatrix} \tag{s8}$$

TABLE S1. Orientation domain variants and the operation in corresponding cosets. All the deduction are based on the pseudo-cubic lattice.

variant type	coset	operations in coset
D_1	$H=P2_1/n$	I, $2[\bar{1}10]$, $\bar{1}$, $m[\bar{1}10]$
D_2	$3^+[111]_c H$	$3^+[111]$, $2[\bar{1}01]$, $\bar{3}^+[111]$, $m[\bar{1}01]$
D_3	$3^+[1\bar{1}\bar{1}]_c H$	$3^+[1\bar{1}\bar{1}]$, $4^+[010]$, $\bar{3}^+[1\bar{1}\bar{1}]$, $\bar{4}^+[010]$
D_4	$3^+[\bar{1}1\bar{1}]_c H$	$3^+[\bar{1}1\bar{1}]$, $4^-[010]$, $\bar{3}^+[\bar{1}1\bar{1}]$, $\bar{4}^-[010]$
D_5	$3^+[\bar{1}\bar{1}1]_c H$	$3^+[\bar{1}\bar{1}1]$, $2[101]$, $\bar{3}^+[\bar{1}\bar{1}1]$, $m[101]$
D_6	$3^-[111]_c H$	$3^-[111]$, $2[01\bar{1}]$, $\bar{3}^-[111]$, $m[01\bar{1}]$
D_7	$3^-[1\bar{1}\bar{1}]_c H$	$3^-[1\bar{1}\bar{1}]$, $4^+[100]$, $\bar{3}^-[1\bar{1}\bar{1}]$, $\bar{4}^+[100]$
D_8	$3^-[\bar{1}1\bar{1}]_c H$	$3^-[\bar{1}1\bar{1}]$, $4^-[100]$, $\bar{3}^-[\bar{1}1\bar{1}]$, $\bar{4}^-[100]$
D_9	$3^-[\bar{1}\bar{1}1]_c H$	$3^-[\bar{1}\bar{1}1]$, $2[011]$, $\bar{3}^-[\bar{1}\bar{1}1]$, $m[011]$
D_{10}	$2[001]_c H$	$2[001]$, $2[110]$, $m[001]$, $m[110]$
D_{11}	$2[010]_c H$	$2[010]$, $4^-[001]$, $m[010]$, $\bar{4}^-[001]$
D_{12}	$2[100]_c H$	$2[100]$, $4^+[001]$, $m[100]$, $\bar{4}^+[001]$

TABLE S2. Transformation matrices of the orientation domain variants

type	matrix	type	matrix
M_1	$\begin{pmatrix} 1/2 & -1/2 & 0 \\ 1/2 & 1/2 & 0 \\ 0 & 0 & 1 \end{pmatrix}$	$M_7=3^-[1\bar{1}\bar{1}]M_1$	$\begin{pmatrix} -1/2 & -1/2 & 0 \\ 0 & 0 & 1 \\ -1/2 & 1/2 & 0 \end{pmatrix}$
$M_2=3^+[111]M_1$	$\begin{pmatrix} 0 & 0 & 1 \\ 1/2 & -1/2 & 0 \\ 1/2 & 1/2 & 0 \end{pmatrix}$	$M_8=3^-[\bar{1}1\bar{1}]M_1$	$\begin{pmatrix} -1/2 & -1/2 & 0 \\ 0 & 0 & -1 \\ 1/2 & -1/2 & 0 \end{pmatrix}$
$M_3=3^+[1\bar{1}\bar{1}]M_1$	$\begin{pmatrix} 0 & 0 & -1 \\ -1/2 & 1/2 & 0 \\ 1/2 & 1/2 & 0 \end{pmatrix}$	$M_9=3^-[\bar{1}\bar{1}1]M_1$	$\begin{pmatrix} 1/2 & 1/2 & 0 \\ 0 & 0 & -1 \\ -1/2 & 1/2 & 0 \end{pmatrix}$
$M_4=3^+[\bar{1}1\bar{1}]M_1$	$\begin{pmatrix} 0 & 0 & 1 \\ -1/2 & 1/2 & 0 \\ -1/2 & -1/2 & 0 \end{pmatrix}$	$M_{10}=2[001]M_1$	$\begin{pmatrix} -1/2 & 1/2 & 0 \\ -1/2 & -1/2 & 0 \\ 0 & 0 & 1 \end{pmatrix}$
$M_5=3^+[\bar{1}\bar{1}1]M_1$	$\begin{pmatrix} 0 & 0 & -1 \\ 1/2 & -1/2 & 0 \\ -1/2 & -1/2 & 0 \end{pmatrix}$	$M_{11}=2[010]M_1$	$\begin{pmatrix} -1/2 & 1/2 & 0 \\ 1/2 & 1/2 & 0 \\ 0 & 0 & -1 \end{pmatrix}$
$M_6=3^-[111]M_1$	$\begin{pmatrix} 1/2 & 1/2 & 0 \\ 0 & 0 & 1 \\ 1/2 & -1/2 & 0 \end{pmatrix}$	$M_{12}=2[100]M_1$	$\begin{pmatrix} 1/2 & -1/2 & 0 \\ -1/2 & -1/2 & 0 \\ 0 & 0 & -1 \end{pmatrix}$

TABLE S3. Transformation relations of domain variants.

I	$2[\bar{1}10]$	$m[\bar{1}10]$	$\bar{1}$
D_1	D_1	D_1	D_1
D_2	D_6	D_6	D_6
D_3	D_8	D_8	D_7, D_4
D_4	D_7	D_7	D_3, D_8
D_5	D_9	D_9	D_9
D_6	D_2	D_2	D_2
D_7	D_4	D_4	D_3, D_8
D_8	D_3	D_3	D_4, D_7
D_9	D_5	D_5	D_5
D_{10}	D_{10}	D_{10}	D_{10}
D_{11}	D_{12}	D_{12}	D_{12}
D_{12}	D_{11}	D_{11}	D_{11}

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