

# Twinning in $\theta$ Alumina Investigated with High Resolution Transmission Electron Microscopy

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## Abstract

$\theta$  alumina obtained by dehydration of boehmite at about 1200°C for 3 h was investigated by HRTEM. The major characteristics of the microstructure are the multiple twinned lamellae arranged along the [001] direction. The width of these lamellae changes from half a  $\theta$  alumina unit cell to several unit cells. The lamellae were observed either to form ledges along the [100] direction or to be terminated within the twinned lamellae. Polytypism resulting from repetitive twinning has been found leading to a variety of periodic arrays having a repeat along the  $c$  axis of  $n \times 0.59$  nm. The polytype with  $n = 2$  was determined by electron diffraction to have an orthorhombic structure. © 1998 Published by Elsevier Science Limited.

## 1 Introduction

Due to potential application in the fields from catalysts to laser coatings, aluminas have been the subject of investigation for a long time. The dehydration of boehmite at high temperature ( $\sim 1200^\circ\text{C}$ ) does not immediately result in the formation of corundum ( $\alpha\text{-Al}_2\text{O}_3$ ), the thermodynamically stable structure. A number of metastable oxides are produced as transition phases before conversion to  $\alpha\text{-Al}_2\text{O}_3$  takes place.  $\theta$  alumina is one of them.<sup>1–3</sup> Although these transition aluminas have been known for many years, their structures are still not fully understood as the grain size of the crystallites does not exceed 300 nm in most cases and thus makes it difficult to identify the detailed

structure unambiguously by single crystal X-ray techniques. Based on the reports,  $\theta$  alumina, an isostructure of  $\beta\text{-Ga}_2\text{O}_3$ , has a monoclinic unit cell with lattice parameters of  $a = 0.562$ ,  $b = 0.2906$ ,  $c = 1.179$  nm,  $\beta = 103.79^\circ$  and space group  $A2/m$ .<sup>4</sup> In comparison with  $\gamma$  and  $\delta$  alumina, the average co-ordination in  $\theta$  alumina is lower and results in a lower density. The volume per  $\text{Al}_2\text{O}_3$  unit in the  $\gamma$ ,  $\delta$  and  $\theta$  phases are  $46.22\text{Å}^3$ ,  $46.33\text{Å}^3$  and  $46.75\text{Å}^3$ , respectively. Electron diffraction and high resolution transmission electron microscopic studies have depicted the presence of twinning in  $\theta$  alumina as being the major characteristic of the microstructure of the  $\theta$  phase. But the details of this twinning have not yet been completely understood.<sup>5–9</sup> The present study is aimed at characterizing the microstructure of  $\theta$  alumina using HRTEM with focus on polytypes formation due to repetitive twinning.

## 2 Experimental

The details of preparation of alumina powder from boehmite dehydrated at 1200°C for 3 h with additives of barium oxide at trace level have been reported elsewhere.<sup>10</sup> X-ray diffraction showed coexistence of  $\gamma$ -,  $\delta$ -,  $\theta\text{-Al}_2\text{O}_3$  and  $\text{BaO}\cdot 6\text{Al}_2\text{O}_3$ . The powder was dispersed in absolute alcohol using ultrasonic stirring and put on a carbon film supported by a copper grid. HRTEM was undertaken to examine the microstructure at ultrafine scale. A JEOL-4000EX/II transmission electron microscope equipped with a top-entry goniometer stage with tilt angle of  $30^\circ$  in both  $X$  and  $Y$  axes was used at 400 kV with focus on revealing the detailed structure of transition aluminas, especially the twinning in  $\theta$  alumina and structural alternation resulting from twinning such

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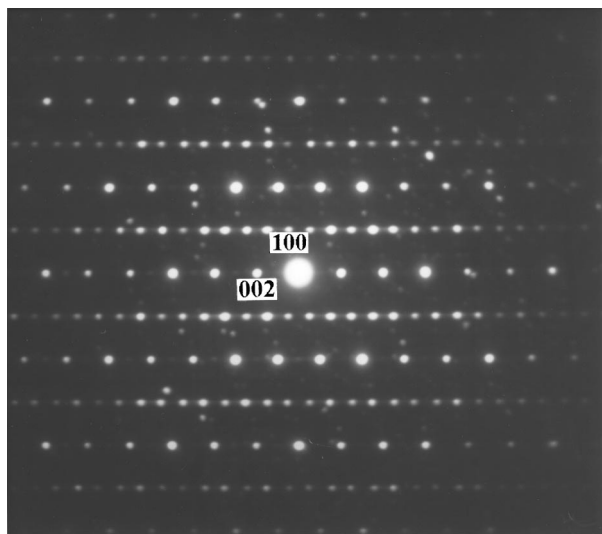
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as polytypism. High resolution micrographs were recorded at a direct magnification of  $5 \times 10^5$  times. The exposure times were chosen as short as possible, usually less than 2 s, in order to avoid specimen drift due to mechanical and electrical instability. Crystals with  $\langle 010 \rangle$  orientations were selected so that the images always include the (100) and (001) planes, which makes it easy to identify the arrangement of the twinning.

### 3 Results and Discussion

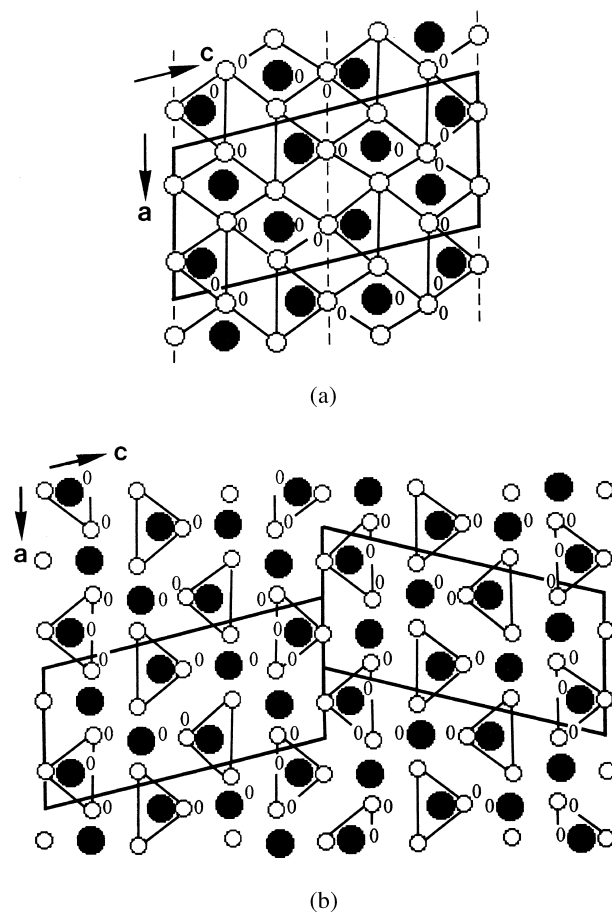
#### 3.1 Twinning in $\theta$ alumina

Twinning is well-developed in  $\theta$  alumina and easy to detect. Figure 1 is an electron diffraction pattern with the electron beam incident along the  $[0\bar{1}0]$  zone axis of the  $\theta$  phase. The twinning characteristics are obvious due to the coexistence of two sets of reflections corresponding to the same structure in two different arrangements. The two sets of reflections sharing the common 001 row suggest that the twinning concerns the (001) plane. The streaking along the  $[001]^*$  direction was always visible in the patterns. Although there are no reported crystal data of  $\theta$  alumina obtained by single crystal X-rays diffraction, such a twinning can be analyzed based on the fundamental structure of  $\beta\text{-Ga}_2\text{O}_3$  because  $\theta$  alumina is an isostructure with  $\beta\text{-Ga}_2\text{O}_3$ .<sup>4</sup> Figure 2(a) is the  $[0\bar{1}0]$  projected structure of  $\beta\text{-Ga}_2\text{O}_3$ . In  $\beta\text{-Ga}_2\text{O}_3$  atoms only occupy positions at heights 0 and 1/2 along the  $b$  axis. The oxygen ions are arranged in a distorted cubic close packed array and form distorted tetrahedra and highly distorted octahedra. A tetrahedron shares only corners with other tetrahedra



**Fig. 1.** An electron diffraction pattern with incident beam projected along the  $[0\bar{1}0]$  direction showing twinning in  $\theta$  alumina. Streaking perpendicular to the (001) plane is clearly visible.

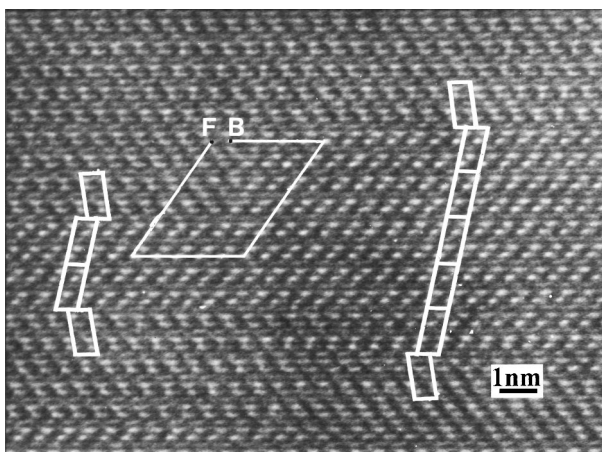
along the  $b$ -axis direction and with octahedra in other directions. An octahedron shares edges with adjacent octahedra in the  $b$ -axis direction and in roughly the  $\langle 201 \rangle$  direction. The cations are surrounded by distorted tetrahedra and octahedra, respectively. The tetrahedrally and octahedrally co-ordinated cations alternatively located at the  $\{201\}$  planes form a layer-like stacking sequence. Careful analysis of the arrangement of the atoms in this structure makes it reasonable to assume that the twinning is based on the operation of a mirror reflection parallel to the (001) plane through the oxygen atoms located near the middle or the end position of the  $c$  axis as indicated by the dashed lines in the figure and followed by a glide of  $\sim 6a/13$ . The position of the oxygen atoms close to the mirror plane should be slightly adjusted to lie on the mirror plane in order to make this relation exact. It is then possible to reflect the whole structure through this mirror plane and translate it parallel to the mirror plane without altering the relative positions of neighbouring atoms at the



**Fig. 2.** (a) The  $[0\bar{1}0]$  projected structure of  $\beta\text{-Ga}_2\text{O}_3$ . The twin planes are indicated by the dashed lines. (b) The structure model of twinning, the closed and open circles represent gallium and oxygen atoms respectively. Unit cells in twin orientation and tetrahedra are indicated for better understanding of twinning. The atoms at zero height along the  $b$  axis are indicated by a number. Other atoms without indication are located at height 1/2.

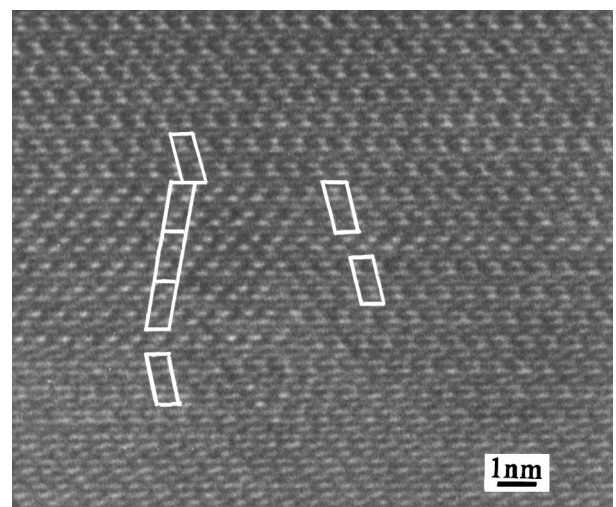
twin boundary. So the twinning is formed by the operation of a glide plane symmetry with a translation  $\sim 6a/13$ . Figure 2(b) shows a possible (001) twin structure built in this way. The tetrahedrally and octahedrally co-ordinated cation layers change from the (201) plane in the matrix to the (101) plane across the twin interface. It should be pointed out that this twin structure can also be constructed by the operation of a  $180^\circ$  rotation parallel to the [100] direction through the oxygen atoms at height 0 located at the same positions as the mirror planes and a translation of  $\sim 6a/13$ . Therefore the twinning shown in Fig. 2(b) can be introduced by either the operation of mirror plane symmetry across the (001) plane with a translation of  $\sim 6a/13$  or a two fold rotation operation along the [100] direction combined with the same translation. Two sets of twin planes are marked in Fig. 2(a). The same twinning can be equally well introduced at these two planes. The difference between the twin structures is only the displacement of the atoms along the b axis at the twin planes.

The corresponding high resolution image (Fig. 3) exhibits the details of the twinning at sub-cell level by intergrowth of lamellae. These lamellae have different width along the [001] direction and are askew with the (001) mirror planes. For easy comparison some unit cells of  $\theta$  alumina are outlined in the twinned regions. There is about an  $a/2$  relative shift between them at the twin interface. The characteristics of the twin configuration confirms the suggested structural model derived by the mirror symmetry across the (001) plane with a translation  $\sim 6a/13$  or a  $180^\circ$  rotation with the same translation along the [100] axis. Multiple twinned lamellae intergrown coherently on the (001) planes are in physical disorder and cause the

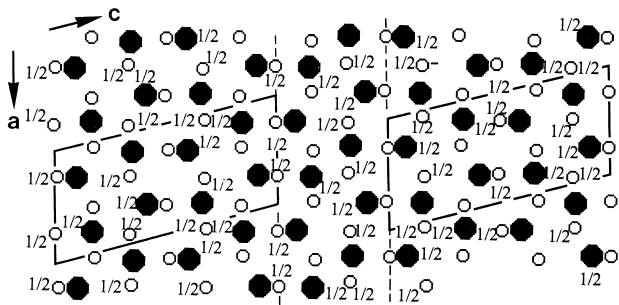


**Fig. 3.** High resolution image showing the twinned lamellae. The width of the lamellae with opposite skews changes from top to bottom. The displacement vector relating the transformation between the twinned  $\theta$  aluminas is determined by drawing a Burgers circuit, around one such twinning point halfway two monoclinic unit cells with angle  $\beta = 103.79^\circ$ .

marked [001]\* streaking in the diffraction pattern. The width of the twinned lamellae is not larger than 10 nm and varies from left to right. The layer on the left with a width of two unit cells becomes five cells wide on the right as indicated. So that twin ledges must be formed along the [100] direction with the boundaries parallel to approximately the (102) plane of the matrix. Burgers vectors relating to the twin transformation along the [100] direction can be measured by a Burgers circuit in the high resolution image:  $0.9a$  was found. The mechanism of transformation between the twinned  $\theta$  phases corresponds to shear parallel to the [100] axis, centered around the (001) plane. A possible Burgers vector for this transformation is examined to be  $2c \sin 13^\circ$ , which coincides with the experimentally measured value of  $0.9a$ . The formation of the twinning is due to migration of cations and coincident with nucleation and growth. In Fig. 3 the twin lamellae all have an integer unit cells width, which means that the twin interfaces are all located on the identical plane. The other plane of possible twinning is indicated in Fig. 2(a). If the twinning happens at the two types of twin planes alternatively, the twin layer with noninteger unit cell width will be introduced. High resolution imaging (Fig. 4) shows the multiple twin lamellae with noninteger unit cell width. On the left hand side the width of the twin band is three and a half unit cells, whereas on the right it reduces to half a unit cell. In this case the  $\theta$  alumina twins on a subunit cell scale. Fig. 5 shows a structure model of such half a unit cell twinning. In this case the oxygen atoms on the one interface is at height  $1/2$  and on the other interface at zero height. Thus the two twin interfaces are not identical because the  $b/2$  relative shift is introduced for the oxygen atoms at these two twin interfaces.



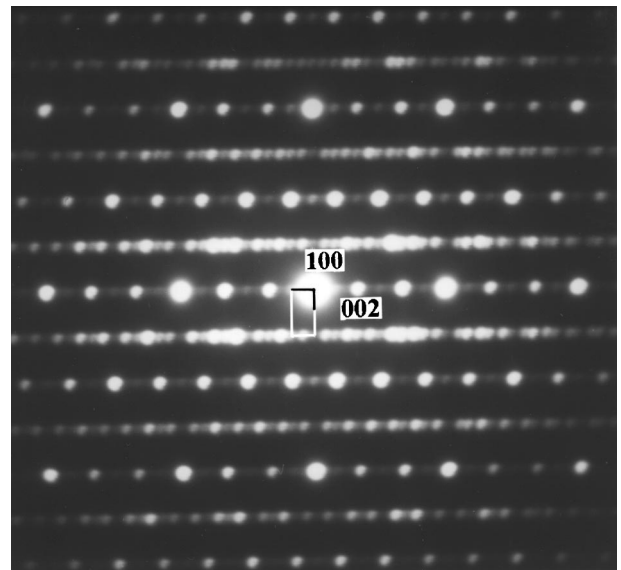
**Fig. 4.**  $[0\bar{1}0]$  high resolution image depicting the twinned lamellae with noninteger unit cell width.



**Fig. 5.** The structure model suggested for the twinned lamellae with half a unit cell width. The two twin interfaces are indicated by dashed lines. The closed and open circles represent aluminium and oxygen atoms, respectively. The atoms at one half height along the b-axis are indicated by a number. Other atoms without indication are located at height zero.

### 3.2 Polytypes due to repetitive twinning

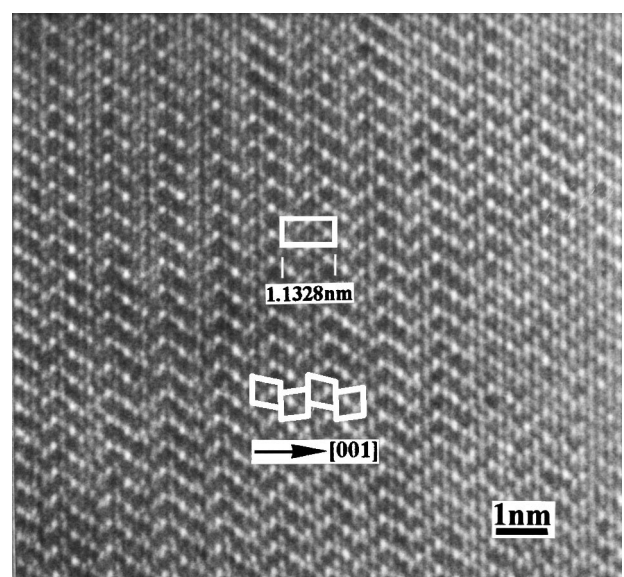
Essentially, polytypism is defined as one dimensional polymorphism. The important differences between polytypes accrue along one crystallographic axis. These differences are produced by varying the stacking sequences of structurally and chemically similar units. Dimensional relationships perpendicular to the stacking direction are almost constant.<sup>11</sup> There are many methods to vary the stacking sequence. Twinning used as an operation for alternation of the stacking sequence along the twin plane normal is one of them. A number of polytypes introduced by polysynthetic twinning in the parent phase have been reported.<sup>12,13</sup> The polysynthetic twinning as a structure building operation happens on the unit cell level, the so-called unit cell twinning is obtained. Unit cell twinning simply means that the periodicity of the twin planes determines the size of the unit cell and the orthorhombic pyroxene constructed by monoclinic pyroxene twinned on a unit cell scale is a good example.<sup>11</sup> Such polysynthetic twinning has also been observed in  $\theta$  alumina by the presence of multiple twinned lamellae. As indicated in Fig. 2(a) there are two sites for the twin boundary. In contradistinction with pyroxene there are two kinds of twin blocks to be chosen. One is the twin interface as shown in Fig. 3. In this case the basic structure building block for polysynthetic twinning is an integer number of unit cells of the  $\theta$  phase. The smallest block is a unit cell and the periodicity of the polytypes is obtained by multiplication of 1.13 nm in the direction perpendicular to the twin plane. The other is the twin interface as shown in Fig. 4. In this case the basic structure building block for polysynthetic twinning becomes a non-integer number of unit cells of the  $\theta$  phase. The smallest one equals half a unit cell and the periodicity of the polytypes is obtained by multiplication of 0.57 nm in the direction parallel to the twin plane normal. Taking these two cases into



**Fig. 6.**  $[0 \bar{1} 0]$  electron diffraction pattern showing the presence of a new polytype in  $\theta$  alumina. The orthorhombic unit cell in reciprocal space is outlined.

consideration the periodicity of the polytypes introduced by polysynthetic twinning in the  $\theta$  alumina can be predicted to be  $n \times 0.57$  nm, where  $n$  is an integer and equals 2, 3, 4, etc.

Figure 6 is an electron diffraction pattern with the electron beam projected along the same direction as in Fig. 1  $[0 \bar{1} 0]$ . Besides the two sets of reflections encountered before from the twinning there is an extra set of reflections forming an orthorhombic lattice as outlined in this pattern. The presence of a new polytype in the  $\theta$  phase is demonstrated by the extra reflections appearing mid-way between the transmitted beam and the 002 reflection and at the rational positions



**Fig. 7.** The corresponding high resolution image showing the polytype with periodicity of 1.13 nm along the (001) plane normal, which is introduced by the twinned plate with half a unit cell width as marked.

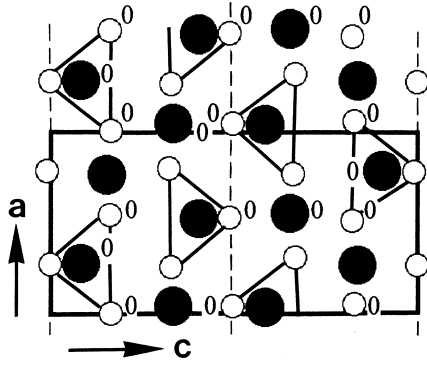


Fig. 8. The proposed structure model for the polytype introduced by polysynthetic twinning as shown in Fig. 7. The twin planes are indicated by dashed lines.

between the 000 and the  $40\bar{2}$  reflections of the matrix. The stacking periods of this new polytype are suggested to be 0.56 and 1.13 nm or multiplication thereof along the [100] and (001) plane normal, respectively. Its lattice may be orthorhombic. Figure 7 shows the corresponding high resolution image. The important characteristic of this micrograph is the very well developed polysynthetic twinning. The interval between the twin planes is examined to be 0.57 nm along the twin interface normal and thus the twin interfaces alternate and are coincident with the aforementioned second set of twin planes. Figure 8 shows the suggested structure model for this polytype. The basic block for the polysynthetic twinning equals half a unit cell of the  $\theta$  alumina and is the smallest

twin unit. This polytype exhibits thus unit cell twinning with a dimension of  $a = 0.56$ ,  $b = 0.29$  and  $c = 1.13$  nm. The  $c$  axis length of this polytype is the same as the (001) planar distance of the  $\theta$  phase. The periodicity of the polytypes due to repetitive twinning has been formalized and this unit cell twinning corresponds to  $n = 2$ . Figure 9 shows the intergrowth of several polytypes with periodicities of 1.13, 1.70, 2.83 and 2.27 nm, corresponding to  $n = 2, 3, 4$  and 5, respectively. For  $n = 4$  the two twin interfaces are on identical planes but not so for the others.

#### 4 Conclusions

We have analysed the twinning in the  $\theta$  alumina with the isostructure of  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> as a starting point. The corresponding structure model was confirmed by an excellent agreement with the experimental observation. In particular the presence of two sets of twin planes introduces an interesting variation in width of the twinned lamellae from integer unit cell width to noninteger unit cell width. It is clear now that although highly localized structural features of  $\theta$  alumina are complex, many of them can be interpreted in terms of twinning. These disordered or locally ordered regions are presumably frozen-in stages during the phase transition from  $\delta$ -  $\rightarrow$   $\theta$ -  $\rightarrow$   $\alpha$ -Al<sub>2</sub>O<sub>3</sub>.

Another feature of structural significance is the ordering of the twinned lamellae. The regular

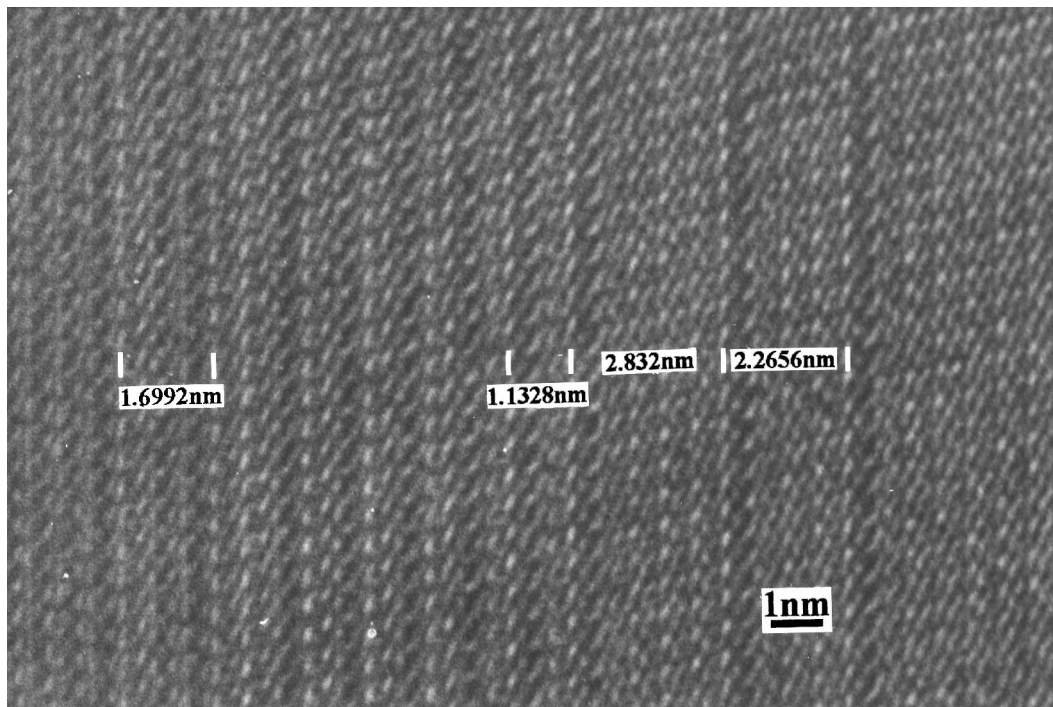


Fig. 9. [010] high resolution image showing intergrowth of the polytypes with periodicity of 1.13, 1.70, 2.27 and 2.83 nm parallel to the twin interfaces.

arrangement of such lamellae in  $\theta$  alumina shows clearly the physical basis of its polytype formation. The relatively short-range (several nanometers) fluctuations in the orientation of lamellae indicate the case with which highly localized deviation from an ideal stacking sequence in the  $\theta$  phase may occur. Such deviations are probable the result of migration of cations during the phase transition. The cations migrate and reorder during this process. They are free to some extent to occupy the octahedral as well as tetrahedral sites. Observations reveal that the plate with only half a unit cell width along the [001] direction could stack in the twinned orientation with respect to the adjacent layers very periodically. Therefore the basic structural building block for unit cell twinning can be visualized as a layer with half a unit cell width along the [001] direction. Localized regular variation of the orientation of the half unit cell width layers introduces a new phase, unit cell level twinning. The new polytype is easy to detect in diffraction pattern, which also shows that the phase has a simple relationship with the matrix, the anion lattice is always conserved. In this study a number of polytypes derived from the  $\theta$  phase by polysynthetic twinning on the unit cell level has been revealed. They are obtained in the same way as macroscopic twinning, with the same definition of twin plane and twin axis. Several sorts of polytypic variation in the  $\theta$  phase and the way that the polytype was initiated have been investigated. Ordering of the twin interfaces in the matrix form a lattice modulation wave that modifies the fundamental

structure perpendicular to the (001) plane and, as a result, new polytypes with repeat periods of  $2\times$ ,  $3\times$ ,  $4\times$  and  $5\times 0.566$  nm may be introduced.

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