

References

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Twin Boundaries in Perovskite

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Abstract

The twin behaviour of natural and synthetic perovskite (CaTiO₃) was examined by high-resolution electron microscopy (HREM) and selected-area electron diffraction (SAD). Pseudosymmetric twinning yields domains related to each other by either a 180° or a 90° rotation about an axis perpendicular to {101}. A third type of twin involving a 180° rotation about the normal to (121) had previously been reported but this was not observed in the present study. The boundaries between twin domains were often complex and consisted of intergrowths on the finest possible scale of the various composition planes. It was confirmed that the most common composition planes were {101}; however, interface surfaces on {010} and {121} were also observed. For the simpler twin boundaries structural models were proposed and described using the Glazer notation.

Introduction

The mineral perovskite (CaTiO₃) is the prototype of the important *perovskite* structural family whose generic stoichiometry is ABX₃. Although initially suggested to be cubic it was soon recognized that CaTiO₃ possessed lower symmetry (Bowman, 1908, and references therein). Subsequent X-ray crystallographic analyses by Megaw (1946) and Kay & Bailey (1957) revealed it to be orthorhombic *Pcmm* with lattice dimensions $a = 5.37 (= \sqrt{2}a')$, $b = 7.64 (= 2a')$, $c = 5.44 (= \sqrt{2}a')$ Å. The relation between the supercell

and the pseudocubic subcell is given by

$$\begin{pmatrix} a \\ b \\ c \end{pmatrix} = \begin{pmatrix} \frac{1}{2} & 0 & \frac{1}{2} \\ 0 & \frac{1}{2} & 0 \\ \frac{1}{2} & 0 & -\frac{1}{2} \end{pmatrix} \begin{pmatrix} a_1 \\ a_2 \\ a_3 \end{pmatrix}.$$

The present transmission-electron-microscope investigation was initiated as part of a study of SYNROC, a titanate phase assemblage designed to immobilize high-level nuclear waste (Ringwood *et al.*, 1981). Perovskite is a major constituent of this waste form.

Experimental methods

Both natural* and synthetic perovskites were examined by selected-area diffraction (SAD) and high-resolution electron microscopy (HREM). The synthetic specimens were obtained by either cold pressing and sintering at 1573 K for 16 h in a CO/CO₂ atmosphere or hot pressing at 14 MPa and 1583 K for 3 h. Perovskite as a component of SYNROC was argon ion-beam milled and examined as self-supporting foils. All other samples were prepared for study by grinding under ethanol with an agate mortar and pestle. Several drops of the suspension were placed on a holey-carbon film mounted on a copper grid. Crystallites were viewed in [010] and [h0l] zones.

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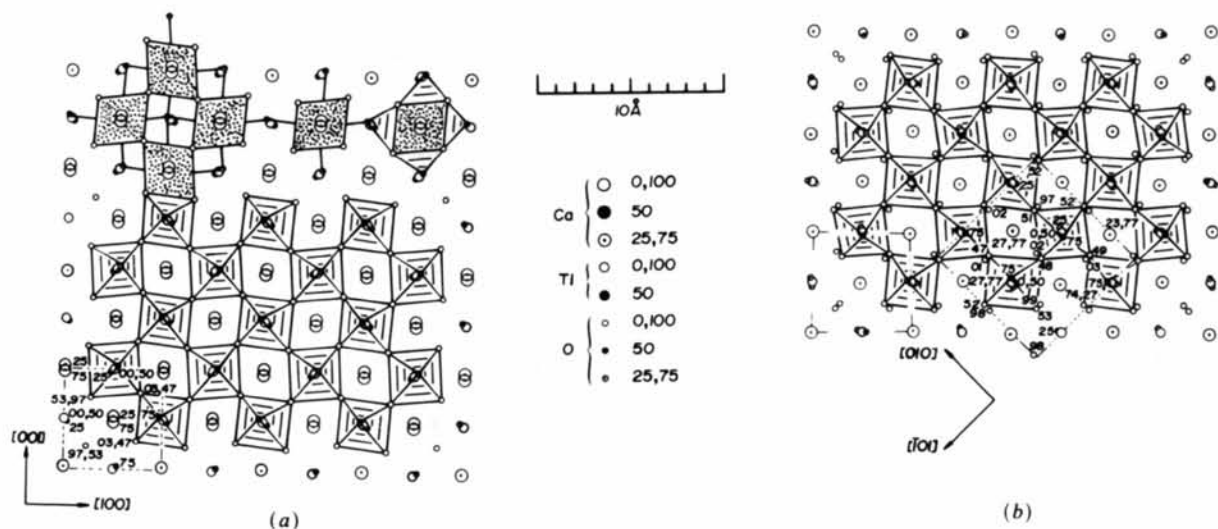


Fig. 1. (a) The perovskite structure projected down the $[0\bar{1}0]$ axis. In the lower portion of the drawing the TiO_6 octahedra are emphasized. The upper section shows columns of face-sharing CaO_{12} tetracapped rhombic prisms. The top right-hand corner of the drawing contains a Ca polyhedron drawn as a heavily distorted cuboctahedron. (b) The $[101]$ zone. Note that the major difference between the two projections down the pseudo-fourfold axes is the displacement of Ca atoms along $[001]$.

Observations were made with a JEOL 100C microscope operated at 100 keV or a JEOL 200CX microscope at 200 keV.

The perovskite structure

The structure of CaTiO_3 departs only slightly from the cubic $Pm\bar{3}m$ aristotype (Lefkowitz, Lukaszewicz

& Megaw, 1966); the obliquity of the pseudocubic subcell ($a = c = 3.83$, $b = 3.82$ Å) is 0.70° . The TiO_6 octahedra form a three-dimensional network whose topography is that of the ReO_3 type whilst the Ca atoms occupy large interstices between the octahedra. Projections down $[0\bar{1}0] = [010]_{pc}$ and $[101] = [001]_{pc}$ emphasize the pseudocubic symmetry (Figs. 1a, 1b) (pseudocubic settings are indicated by the subscript pc). Oxygen displacements leave the octahedra essentially undistorted but rotated by 11.8° about $\langle 111 \rangle_{pc}$ to produce a bioctahedral repeat period (O'Keeffe & Hyde, 1977).* The partial 'collapse' of the octahedral framework reduces the size of the A interstices and to satisfy Ca-O bond criteria the Ca atoms are displaced 0.23 Å along $[001]$ (Kay & Bailey, 1957). Consequently, each Ca atom has eight near and four next-nearest O neighbours; the coordination polyhedron can be considered as a distorted cuboctahedron, or, more descriptively, a tetracapped rhombic prism (Nyman, 1976).

Twinning

The optical microscope and X-ray diffraction studies of Bowman (1908) and Kay & Bailey (1957) identified three pseudosymmetric rotation twins.

- (1) The most common form involved a rotation of 180° about the normal to $(101) = (001)_{pc}$.
- (2) Twinning by rotation of 90° about an axis normal to (101) was also frequently observed.
- (3) In addition, Bowman described a very rare twin in which the individuals were related by a rotation

* The rotation also incorporates a small secondary tilt about $(100)_{pc}$ (O'Keeffe & Hyde, 1977).

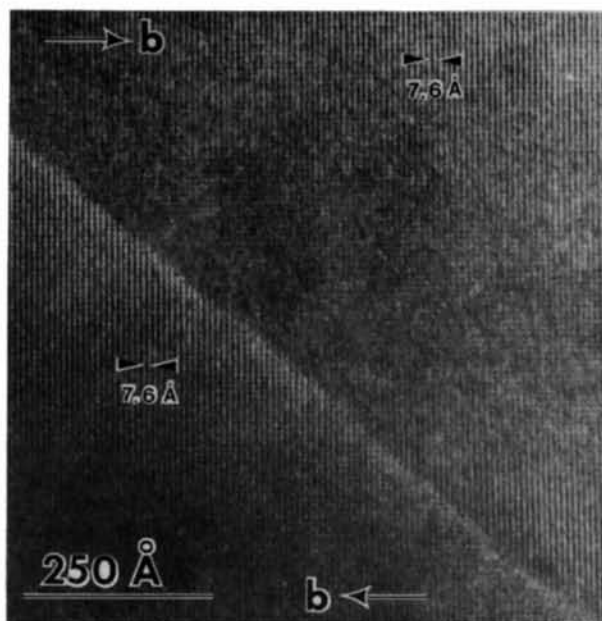


Fig. 2. The contact surface of twin domains related by a 180° rotation about the normal to (101) . The composition plane is approximately $\{121\}$ but the diffuse nature of the boundary is indicative of deviation from the rational high-index interface.

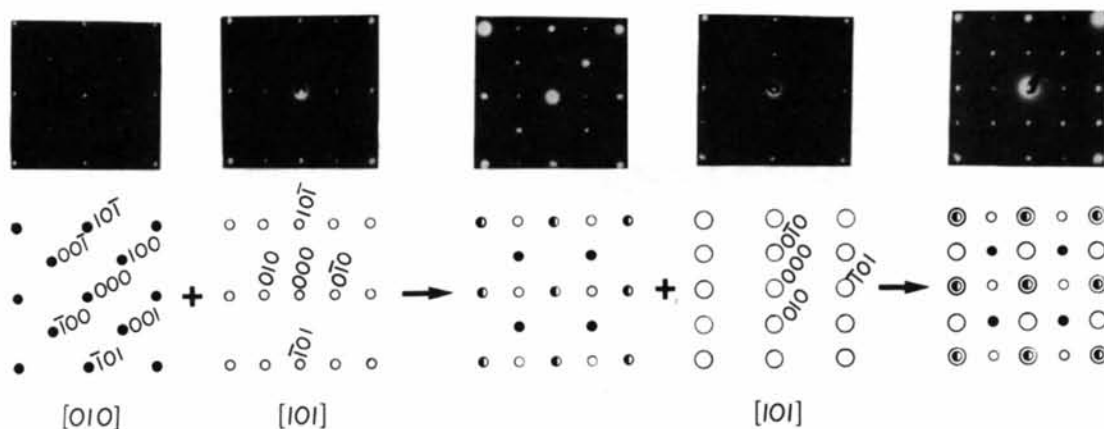


Fig. 3. Selected-area diffraction patterns obtained from crystals twinned by 90° rotation about an axis perpendicular to (101).

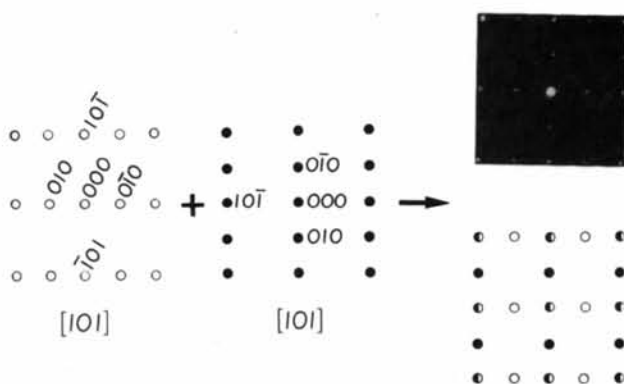


Fig. 3. (cont.)

of 180° normal to $(121) = (110)_{pc}$; however, Kay & Bailey could not unequivocally verify this type.

Although these earlier studies characterized the twin laws that were operating they were unable to provide very much information regarding the interface surfaces thus formed. Our investigations concentrate on this aspect of the microstructure and establish which composition planes occur in perovskite.

Results

180° rotation twin about the normal to $(101) = (001)_{pc}$

Twins of this kind were not recognized in diffraction patterns of the major zones because of the (almost) exact coincidence of the reflections contributed from each individual, but they were visible in HR images. Kay & Bailey reported that the most common interface plane was $\{101\} = \{001\}_{pc}$ and we also observed interfaces of this type. However, they did not explicitly exclude $\{10\bar{1}\} = \{100\}_{pc}$ and the structural equivalence of the $\{101\}$ forms makes it difficult to imagine any constraint which would favour (101) interfaces over $(10\bar{1})$. We also encountered com-

position planes of the form $\{121\}$.^{*} An example is shown in Fig. 2; note that the interface is not sharply delineated, indicating some departure from $\{121\}$. Twin boundary planes on $\{010\} = \{010\}_{pc}$ were very rare but could be recognized as lamellar 'defects' (Fig. 7a).

90° rotation twin about the normal to $(101) = (001)_{pc}$

Kay & Bailey's diagram illustrating the 90° rotation twin shows (101) as the composition plane; however, the implication from their optical microscopy study was that other interfaces occur. Our studies revealed $\{101\}$, $\{010\}$ and $\{121\}$ twin boundary planes. Perovskite domains which were related by this twin law were readily identified by SAD because such patterns yielded pseudospacings of 7.6 \AA (Fig. 3). Fig. 4(a) shows a crystal which rather remarkably displays three recognizable composition planes. This image is represented diagrammatically in Fig. 4(b) where a single octahedral layer is illustrated. The small non-coincidence of the O sites is not shown, but the disparity of the Ca positions is depicted by overlapping circles. Usually, though, the composition planes were not nearly as well defined and complicated overlap regions were observed (Fig. 5).

180° rotation twin about the normal to $(121) = (110)_{pc}$

This twin law was reported by Bowman (1908) from a single chemically etched crystal section of natural perovskite. However, Kay & Bailey were unable to identify it positively in their synthetic specimens. They suggest that the twin, if it occurs at all, will only be found in natural samples which have been subjected to high pressures. Likewise, our specimens (both natural and synthetic) have thus far failed to reveal twins of this type.

* $(1\bar{2}1) = (1\bar{1}0)_{pc}$; $(121) = (110)_{pc}$; $(12\bar{1}) = (01\bar{1})_{pc}$; $(1\bar{2}\bar{1}) = (011)_{pc}$.

The description of twin boundaries

Although the more diffuse twin boundaries (e.g. Fig. 5) are quite complex it is possible to rationalize their description by considering them as intermixtures in

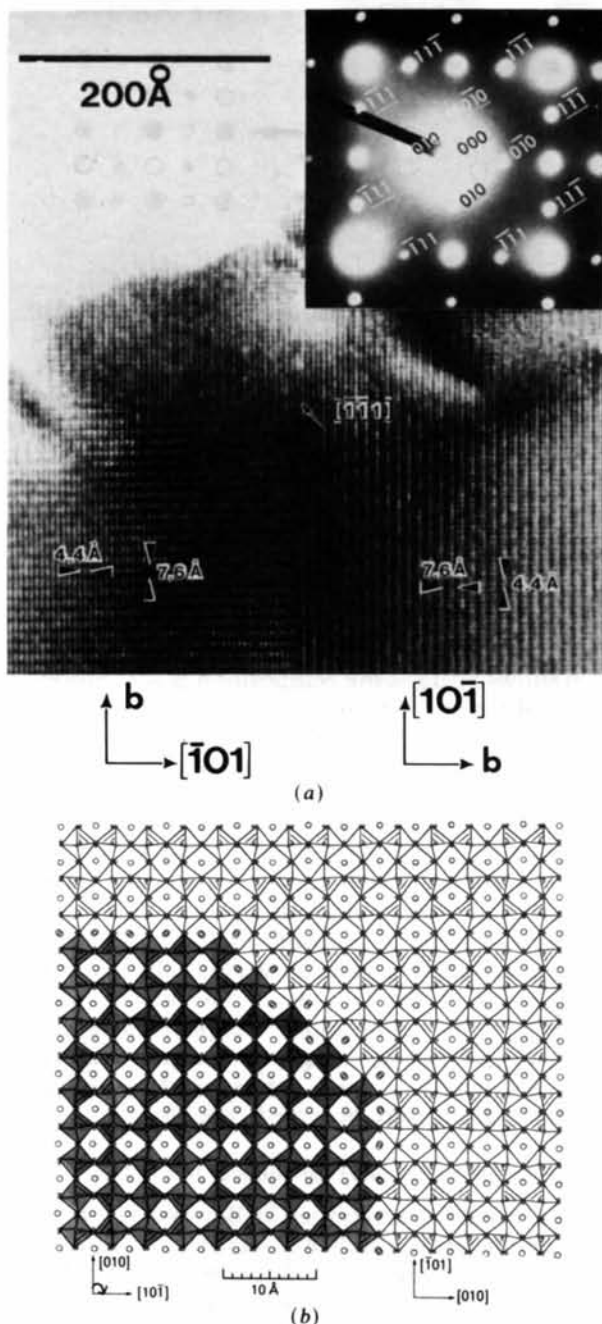


Fig. 4. (a) A twinned perovskite crystallite containing three well defined composition planes approximately parallel to the electron beam; when referenced to the left-hand domain the interface surfaces are (101) , $(10\bar{1})$ and $(1\bar{2}\bar{1})$. (b) Polyhedral diagram of a twinned crystallite containing two domains - the shaded and unshaded regions. The slight mismatch of the O array at the interface is not shown, whilst overlapping circles represent the non-coincidence of the Ca sites; the Ti array is perfectly coherent across the boundary.

three dimensions of a few high-index interface surfaces which, because of their inherent pseudosymmetry, possess sets of 'coincident' sites that are suitable for the formation of low-energy composition planes. Fig. 4(b) illustrates how three different surfaces can be incorporated in a $(10\bar{1})$ octahedral monolayer whilst maintaining (almost) perfect atomic coherency on the plane of contact. It is not difficult to visualize how such boundaries could propagate through a real crystal without destroying the integrity of the octahedral network.

It is particularly pertinent that the environment for the Ca atom (in the parent structure) is established purely by the partial collapse of the regular octahedral framework - the TiO_6 polyhedra remain essentially perfect with the Ti atoms retaining their centrosymmetry. Thus, the octahedra may be considered as structural blocks which remain invariant as they undergo topological distortion. Although the O array is likely to undergo some additional distortion at the composition plane (to accommodate the inevitable displacement of the Ca atoms), one could reasonably expect ReO_3 topography to be maintained across a twin boundary. Indeed, if parent O and Ca arrays are superimposed in orientations consistent with the known twin laws of perovskite (as in Fig. 4b) the maximum mismatch of the 'coincident' sites (in the

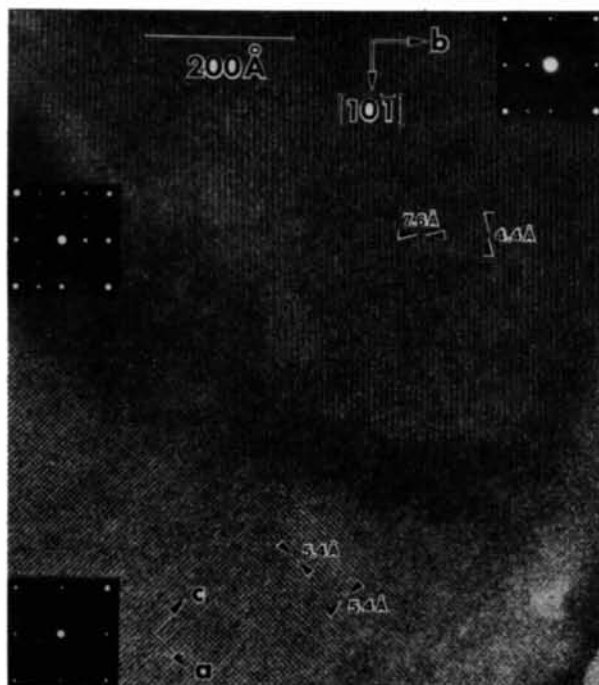


Fig. 5. A high-resolution image of a 90° twin in perovskite. The diffraction patterns at the corners of the image belong to the twin individuals while the central pattern is their composite. The boundary is quite complex as a result of fine-scale intergrowth of the various composition planes.

plane of the drawing) is found to be <0.1 and 0.12 Å respectively. In the composition plane the mismatch of O sites is 0.21 Å. As the Ti atoms are not displaced from their special positions it is anticipated that the Ti array will suffer minimal distortion and should be almost perfectly coherent across the interface.

Since corner connectivity constrains successive octahedra to have opposite tilts about any pseudo-fourfold axis it should be possible to elucidate the tilt arrangement at the twin boundary. In reality such a task is inconceivable for a very complex boundary such as that in Fig. 5. However, for simple examples where the composition plane is well defined and planar it is possible to consider twinning as a means of generating thin, (sometimes) lamellar intergrowths of other perovskite polytypes within the parent structure.

The Glazer notation

A method for describing topological distortions in perovskites was developed by Glazer (1972) who considered the tilt components about the (pseudo) symmetric $\langle 100 \rangle_{pc}$ axes. In this manner he was able to derive 22 tilt systems (with bioctahedral repeats) from the aristotype. Perovskite belongs to a three-tilt system in which two of the tilts are of the same sense and equal magnitude; for the $Pcmm$ setting it has the Glazer symbol $a^-b^+a^-$. To simplify his classification the octahedra were assumed to be regular and cationic displacements were not considered. This is unimportant if a purely qualitative description is required as these perturbations will only alter the symmetry of the tilt system. The scheme is especially applicable to CaTiO_3 since the TiO_6 groups are slightly distorted, the tilt angles small and the displacements of the A cations quite minor. A schematic illustration of the tilt motif of the first octahedral layer of perovskite is shown in Fig. 6(a). Because of A-type centring (i.e. the positions 000 and $0\frac{1}{2}\frac{1}{2}$ are equivalent) the second layer can be simply obtained by reversing the signs of the tilts (Fig. 6b). The sense of tilting can be directly read from Fig. 1(b).

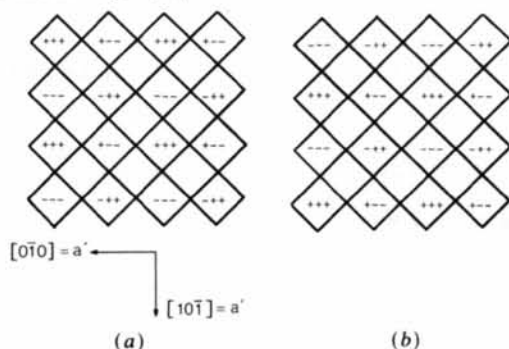
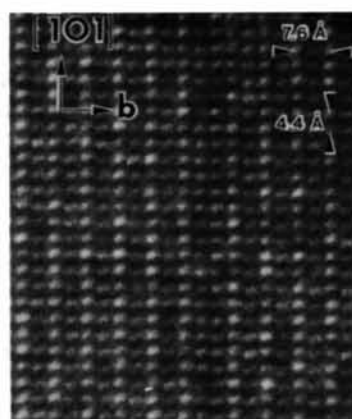
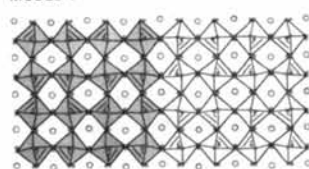


Fig. 6. (a) Schematic illustration of the tilt motif in perovskite using the Glazer notation. The structure is viewed down the pseudo-fourfold $[101]$ axis. (b) The second octahedral layer obtained by reversing the sign of the tilts in (a).

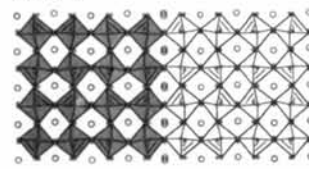


(a)

MODEL 1

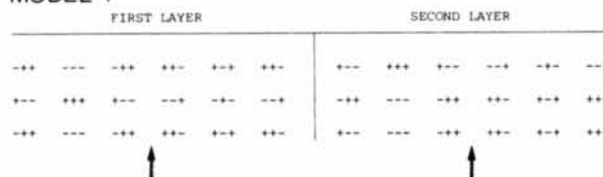


MODEL 2

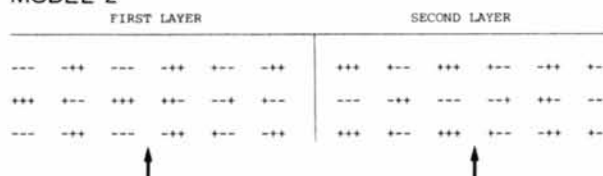


(b)

MODEL 1



MODEL 2



(c)

Fig. 7. (a) A lamellar fault in perovskite. (b) Polyhedral drawings of two possible models for the extended defect. Mismatch of Ca sites in model 2 is indicated by overlapping circles. (c) Schematic illustration of two possible biocathedral tilt patterns generated by 180° rotation twinning.

We suggest that the Glazer notation is particularly suited to the derivation and description of twin boundaries because it provides a concise and unambiguous means of enumerating the various structural models for each composition plane. A single, simple example will serve to illustrate the potential of this system.

Lamellar (twin) boundaries

The simplest boundary which was encountered is shown in Fig. 7(a). The perovskite domains are related to each other by a rotation of 180° about the normal to $(101) = (001)_{pc}$. Only one structure may be postulated in which the Ca, Ti and O positions of the individuals coincide exactly at the interface. This is illustrated by the (single layer) polyhedral drawing in Fig. 7(b) (labelled model 1).

Several other models, which also involve this twin law, are possible. However, in these instances Ca and O displacements are required. One such example (model 2 in Fig. 7b) is given.

Alternatively, these models may be conveniently and completely represented - both octahedral layers are indicated - by listing the octahedral tilt patterns (Fig. 7c); the pseudocubic axes are $a' = [0\bar{1}0]$, $a' = [10\bar{1}]$ and $a' = [\bar{1}0\bar{1}]$. These tilt sequences can be obtained by inspection from drawings of the octahedral motifs.

Discussion

It is interesting that of the several pseudocubic axes present in perovskite only those which involve rotation about $\langle 100 \rangle_{pc}$ are utilized for twinning. However, interface surfaces were observed on planes of the forms $\{101\} = \{001\}_{pc}/\{100\}_{pc}$, $\{010\} = \{010\}_{pc}$ and $\{121\} = \{110\}_{pc}/\{011\}_{pc}$. Not surprisingly, many of the observed twin boundaries were very complicated as a result of extremely fine-scale intergrowth on the several pseudosymmetric interfaces. The variation in octahedral tilt pattern across the composition planes

may simply be considered as a coherent interface between domains of the well known perovskite polytype, or as extremely thin regions of other hettotypes. The latter description is particularly compelling in those instances where lamellar defects are introduced (Fig. 7a).

It is proposed that perovskite in SYNROC will incorporate trivalent rare-earth elements and tetravalent actinide elements (Ringwood *et al.*, 1981). A wide-ranging study of perovskite containing 2-6 at.% of these elements failed to reveal any change in twin behaviour or the presence of cation ordering to yield superstructures.

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Constitution and Structure of Synthetic Hollandites, an Electron and X-ray Diffraction Study

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Abstract

Synthetic hollandite compounds of composition $A_x M_{4-2x}^{IV} N_{2x}^{III} O_8$ ($A = \text{Sr, Ba}$; $M = \text{Ti, Sn}$; $N = \text{Al, Cr, Ga, In}$) studied by electron and X-ray diffraction have been found to be stable only within certain ranges of

x , depending on the M and N ions. The lower value of x is never less than 0.54, the upper x level is about 0.73. Higher x seems to be correlated with larger radii of M and N . The A ions are accommodated along tunnels, giving rise to an incommensurate superstructure. A simple vacancy modulation wave is proposed