International Tables for Crystallography (2013). Vol. D, Figure 3.4.4.4, p. 534.

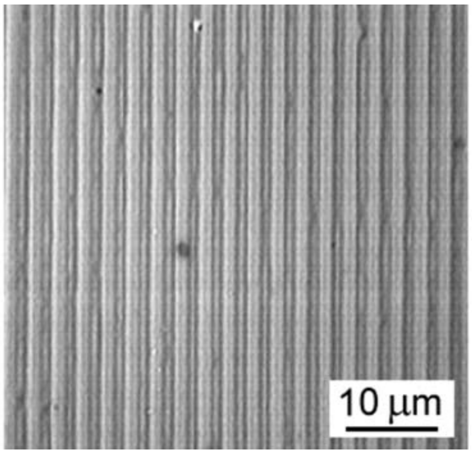

Fig. 3.4.4.3. Engineered periodic non-ferroelastic ferroelectric stripe domain structure within a lithium tantalate crystal with symmetry descent $\bar{6} \supset 3$. The domain structure is revealed by etching and observed in an optical microscope (Shur *et al.*, 2001). Courtesy of Vl. Shur, Ural State University, Ekaterinburg.

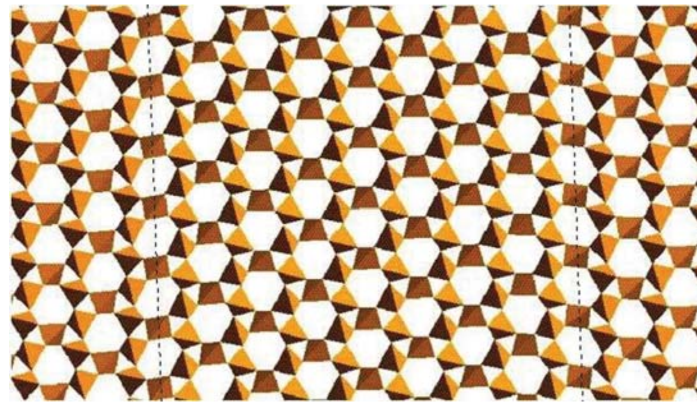

Fig. 3.4.4.4. Microscopic structure of two domain states and two parallel mutually reversed domain walls in the α phase of quartz. The left-hand vertical dotted line represents the domain wall W_{12}, the right-hand line is the reversed domain wall W_{12}. To the left of the left-hand line and to the right of the right-hand line are domains with domain state $\mathbf{S}_1$, the domain between the lines has domain state $\mathbf{S}_2$. For more details see text. Courtesy of M. Calleja, University of Cambridge.

Example 3.4.4.2. Domain walls in the α phase of quartz. Quartz (SiO_2) undergoes a structural phase transition from the parent β phase (symmetry group $6_z2_x2_y$) to the ferroic α phase (symmetry 3_z2_x). The α phase can appear in two domain states $\mathbf{S}_1$ and $\mathbf{S}_2$, which have the same symmetry $F_1 = F_2 = 3_z2_x$. The symmetry J_{12} of the unordered domain pair $\{\mathbf{S}_1, \mathbf{S}_2\}$ is given by $J_{12}^\star = 3_z2_x \cup 2_y^*\{3_z2_x\} = 6_z^*2_x2_y^*$.

Table 3.4.4.5 summarizes the results of the symmetry analysis of domain walls (twins). Each row of the table contains data for one representative domain wall $\mathbf{W}_{12}(\mathbf{n}_{12})$ from one orbit $G\mathbf{W}_{12}(\mathbf{n}_{12})$. The first column of the table specifies the normal $\mathbf{n}$ of the wall plane p, further columns list the layer groups $\widehat{\mathsf{F}}_{12}$, T_{12} and $\overline{\mathsf{J}}_{12}$ that describe the symmetry properties and classification of the wall (defined in Table 3.4.4.3), and n_W is the number of symmetry-equivalent domain walls [*cf.* equation (3.4.4.21)].

The last two columns give possible components of the spontaneous polarization $\mathbf{P}$ of the wall $\mathbf{W}_{12}(\mathbf{n})$ and the reversed wall $\mathbf{W}_{21}(\mathbf{n})$. Except for walls with normals [001] and [100], all walls are polar, *i.e.* they can be spontaneously polarized. The reversal of the polarization in reversible domain walls requires the reversal of domain states. In irreversible domain walls, the reversal of $\mathbf{W}_{12}$ into $\mathbf{W}_{21}$ is accompanied by a change of the polarization $\mathbf{P}$ into $\mathbf{P}'$, which may have a different absolute value and direction different to that of $\mathbf{P}$.

The structure of two domain states and two mutually reversed domain walls obtained by molecular dynamics calculations are depicted in Fig. 3.4.4.4 (Calleja *et al.*, 2001). This shows a projection on the *ab* plane of the structure represented by SiO_4 tetrahedra, in which each tetrahedron shares four corners. The threefold symmetry axes in the centres of distorted hexagonal channels and three twofold symmetry axes (one with vertical orientation) perpendicular to the threefold axes can be easily seen. The two vertical dotted lines are the wall planes p of two mutually reversed walls $[\mathbf{S}_1[010]\mathbf{S}_2] = \mathbf{W}_{12}[010]$ and $[\mathbf{S}_2[010]\mathbf{S}_1] = \mathbf{W}_{21}[010]$. In Table 3.4.4.5 we find that these walls have the symmetry $\mathsf{T}_{12}[010] = \mathsf{T}_{21}[010] = \underline{2}_x2_y^\star\underline{2}_z^\star$, and in Fig. 3.4.4.4 we can verify that the operation $\underline{2}_x$ is a 'side-reversing' operation $\underline{s}_{12}$ of the wall (and the whole twin as wall), operation $2_y^\star$ is a 'state-exchanging operation' $r_{12}^\star$ and the operation $\underline{2}_z^\star$ is a non-trivial 'side-and-state reversing' operation $\underline{t}_{12}^\star$ of the wall. The walls $\mathbf{W}_{12}[010]$ and $\mathbf{W}_{21}[010]$ are, therefore, symmetric and reversible walls.

During a small temperature interval above the appearance of the α phase at 846 K, there exists an incommensurate phase that can be treated as a regular domain structure, consisting of triangular columnar domains with domain walls (discommensurations) of negative wall energy σ (see *e.g.* Dolino, 1985). Both theoretical considerations and electron microscopy observations (see *e.g.* Van Landuyt *et al.*, 1985) show that the wall normal has the [$uv0$] direction. From Table 3.4.4.5 it follows that there are six equivalent walls that are symmetric but irreversible, therefore any two equivalent walls differ in orientation.

This prediction is confirmed by electron microscopy in Fig. 3.4.4.5, where black and white triangles correspond to domains with domain states $\mathbf{S}_1$ and $\mathbf{S}_2$, and the transition regions between black and white areas to domain walls (discommensurations). To a domain wall of a certain orientation no reversible wall appears with the same orientation but with a reversed order of black and white. Domain walls in homogeneous triangular parts of the structure are related by 120 and 240° rotations and carry, therefore, parallel spontaneous polarizations; wall orientations in two differently oriented blocks (the middle of the right-hand part and the rest on the left-hand side) are related by 180° rotations about the axis 2_x in the plane of the photograph and are, therefore, polarized in antiparallel directions (for more details see Saint-Grégoire & Janovec, 1989; Snoeck *et al.*, 1994). After cooling down to room temperature, the wall energy becomes positive and the regular domain texture changes into a coarse domain struc-

Table 3.4.4.5. *Symmetry properties of domain walls in α quartz*

$|\mathbf{P}| \neq |\mathbf{P}'|,\ P_i' \neq -P_i,\ i = x, y, z.$

$\mathbf{n}$	$\widehat{\mathsf{F}}_{12}$	T_{12}	$\overline{\mathsf{J}}_{12}$	Classification	n_W	$\mathbf{P}(\mathbf{W}_{12})$	$\mathbf{P}(\mathbf{W}_{21})$
[001]	3_z	$3_z\underline{2}_y^*$	$6_z^*\underline{2}_x\underline{2}_y^*$	SR	2		
[100]	2_x	$2_x\underline{2}_y^*\underline{2}_z^*$	$2_x\underline{2}_y^*\underline{2}_z^*$	SI	3		
[010]	1	$\underline{2}_z^*$	$\underline{2}_x2_y^*\underline{2}_z^*$	SR	6	$0, 0, P_z$	$0, 0, -P_z$
[$0vw$]	1	1	$\underline{2}_x$	A$\underline{\text{R}}$	12	P_x, P_y, P_z	$P_x, -P_y, -P_z$
[$u0w$]	1	$\underline{2}_y^*$	$\underline{2}_y^*$	SI	6	$0, P_y, 0$	$0, -P_y', 0$
[$uv0$]	1	$\underline{2}_z^*$	$\underline{2}_z^*$	SI	6	$0, 0, P_z$	$0, 0, P_z'$
[uvw]	1	1	1	AI	12	P_x, P_y, P_z	P_x', P_y', P_z'