1 EXERCISE: Phase Transitions of BaTiO$_3$

1.1 Solution

Sketches of the deformed unit cells relative to the cubic cell are given below

Fig. E9.1. Unit cells of the four phases of BaTiO$_3$. (a) cubic, stable above 120°C; (b) tetragonal, stable between 120°C and 5°C; (c) orthorhombic, stable between 5°C and -90°C; (d) rhombohedral, stable below -90°C. The dotted lines in (b), (c), and (d) delineate the original cubic cell. The heavy arrows indicate the direction of the spontaneous polarization $P_s$ in each phase.

(i) (b) Displacement parallel $<100>$: tetragonal
(c) Displacement parallel $<110>$: orthorhombic
(d) Displacement parallel $<111>$: trigonal (rhombohedral).

(ii) (b) Tetragonal polymorph: space group $P4mm$
(c) Orthorhombic polymorph: space group $Amm2$
(d) Rhombohedral polymorph: space group $R3m$ Note that for the orthorhombic cell with axes $\mathbf{a}', \mathbf{b}', \mathbf{c}'$ two axes are chosen along face diagonals of the cubic cell (axes $\mathbf{a}, \mathbf{b}, \mathbf{c}$ and one along a cube edge; for instance, for the diagram (c):

\[ \mathbf{a}' = \mathbf{a}, \mathbf{b}' = \mathbf{b} - \mathbf{c}, \mathbf{c}' = \mathbf{b} + \mathbf{c} \] (polar axis),
resulting in space group $Amm2$ (No. 38).

(iii) The subgroup indices are:

(b) $|\mathcal{G} : \mathfrak{h}| = |Pm3m : P4mm| = 6$ threefold axes lost

(c) $|\mathcal{G} : \mathfrak{h}| = |Pm3m : Amm2| = 12$ fourfold and threefold axes lost

(d) $|\mathcal{G} : \mathfrak{h}| = |Pm\bar{3}m : R\bar{3}m| = 8$ fourfold axes lost.

(iv) For the twinning of BaTiO$_3$ the numbers of orientation states of the domains are equal to the subgroup indices given above. For case (b), tetragonal $P4mm$, there exist three pairs of "90 domains" along the edges of the cubic high-temperature cell, each pair consisting of two "180 domains", due to the antiparallel orientations of the vectors of spontaneous polarisation in the polar space group $P4mm$.

2 EXERCISE: Subgroups of Point Group $4mm$; Translationengleiche Subgroups of Space Groups $P4mm$

2.1 Solution

The point group $4mm$ has order 8: the group elements are $1$, $2_z = 4_2^z$, $4_1, 4_{-1} = 4_3^z, m_x, m_y, m_+$ and $m_-$. The rotations are labelled as in the Fig. 1 in order to describe the subgroups uniquely.

![Diagram of symmetry group $4mm = C_4v$ of the square](image)

Fig.1. Symmetry group $4mm = C_4v$ of the square
Point group 4mm has three subgroups of index [2], i.e. order 4. Their Hermann-Mauguin symbols are 4z, mx, my 2z and m+ m− 2z where 2z is contained in 4z. The five subgroups of index [4], i.e. order 2, are 2z, mx, my, m+ and m−.

Subgroups diagram of 4mm (Fig. 2).

All three subgroups of index [2] (order 4) are normal, of the five subgroups of index [4], 2z is normal (because it has no conjugates in 4mm). The subgroups mx and my, as well as m+ and m− each form a conjugate pair, because my = 4z mx 4z−1 and m+ = 4z m− 4z−1 holds. (In subgroups diagrams conjugation is sometimes indicated by horizontal lines: mx—my and m+—m−).

The diagram in (ii) can be used to display the translationengleiche subgroups of space group P4mm (Fig. 3). For each group the upper symbol indicates those operations of P4mm which are retained in the subgroup, leading to non-standard symbols, e.g. P2z,m1. The lower symbol is the standard (short) Hermann-Mauguin symbol of the subgroups.

Remark 1. Due to the convention to choose the basis vectors parallel to the rotation axes, C-centered cells appear although the translation lattice has not changed. If the retained twofold axes are diagonal, the conventional basis vectors a’, b’, c’ of the subgroup are a’ = a−b, b’ = a+b, c’ = c.
with respect to the basis vectors \( \mathbf{a}, \mathbf{b}, \mathbf{c} \) of \( P4mm \). Referred to \( \mathbf{a}', \mathbf{b}', \mathbf{c}' \) the cell is \( C \)-centered, see Fig.4.

![Change of basis vectors: \( \mathbf{a}' = \mathbf{a} - \mathbf{b}, \mathbf{b}' = \mathbf{a} + \mathbf{b} \)](image)

Changes of lattice-type symbols in subgroup relations are not uncommon. Another example are *translationengleiche* tetragonal subgroups of cubic \( F \) space groups: \( Fm\bar{3}m \rightarrow F4/m\bar{1}2/m \sim I4/mmm \), etc., because there is no standard \( F \) for tetragonal spacegroups in ITA (1983).

Remark 2. The analogy between point group \( 4mm \) and its space groups is not restricted to \( P4mm \) but extends to all twelve space groups of this crystal class, from \( P4mm \) (No. 99) to \( I4/cd \) (No. 110). The 'family trees' are always of the same kind, only the entries differ.

3 EXERCISE: Splitting of Wyckoff positions for the group-subgroup pair \( P4mm > Cm \)

3.1 Solution

Consider group-subgroup related space groups \( \mathcal{G} > \mathcal{H} \). Atoms which are symmetrically equivalent under \( \mathcal{G} \), i.e. belong to the same orbit of \( \mathcal{G} \), may become non-equivalent under \( \mathcal{H} \), i.e. the orbit splits) and/or their site symmetries may be reduced. The orbit relations induced by the symmetry reduction are the same for all orbits belonging to a Wyckoff position, so one can speak of Wyckoff-position relations or splitting of Wyckoff positions. Theoretical aspects of the relations of the Wyckoff positions for a group-subgroup pair of space groups \( \mathcal{G} > \mathcal{H} \) has been treated in detail by Wondratschek (Miner-
alogy and Petrology, \textbf{48}(1993), 87-96). An important result is given by the following lemma:

Let $\mathcal{G}$ be a space group and $\mathcal{H}$ a subgroup of index $[i]$ of $\mathcal{G}$. The site-symmetry groups of a point $X$ under the space group $\mathcal{G}$, $S_\mathcal{G}(X)$ and under its subgroup $\mathcal{H}$, $S_\mathcal{H}(X)$, define the so-called reduction factors of the site symmetry: $R = \frac{|S_\mathcal{G}(X)|}{|S_\mathcal{H}(X)|}$. When the space-group symmetry is reduced from $\mathcal{G}$ to $\mathcal{H}$ and the orbit $O_\mathcal{G}(X)$ of the point $X$ in $\mathcal{G}$ splits into $q$ orbits $O_\mathcal{H}(X_j)$ of $\mathcal{H}$, the following relation holds:

$$[i] = \sum_{j=1}^{q} R_j$$

The maximal splitting corresponds to $R_j = 1$ for each $j = 1, \ldots, q$ and this is always the case if $O_\mathcal{G}(X)$ is a general-position orbit.

The splitting of the Wyckoff positions for the symmetry break $P4mm > Cm$ can be done by direct inspection. For that it is first necessary to transform the coordinates of the Wyckoff positions representatives of $P4mm$ to the subgroup basis. In our specific case, with zero origin shift, the coordinates of a point $(X)_\mathcal{G}$, expressed in the basis of $\mathcal{G}$ are given by:

$$(X)_\mathcal{G} = \mathbf{P}^{-1}(X)$$

Here, the 3x3 square matrix $\mathbf{P} = \| P_{ij} \|$ transforms the conventional basis $(a, b, c)_\mathcal{G}$ of $\mathcal{G}$ to the conventional basis of $\mathcal{H}$:

$$(a', b', c')_\mathcal{H} = (a, b, c)_\mathcal{G} \mathbf{P}$$

The direct inspection of the transformed coordinates of the Wyckoff position representatives and their comparison with the representatives of the Wyckoff positions of $Cm$ gives the following splitting schemes:

$$1a \ 4mm \ (0, 0, z) \rightarrow 2a \ m \ (x, 0, z)$$

$$1b \ 4mm \ (1/2, 1/2, z) \rightarrow 2a \ m \ (x, 0, z)$$

$$2c \ 2mm \ (1/2, 0, z) \rightarrow 4b \ l \ (x, y, z)$$

$$4d \ . \ m \ (x, x, z) \rightarrow 4b \ l \ (x, y, z) \cup 2a \ m \ (x, 0, z) \cup 2a \ m \ (x, 0, z)$$

No splittings occur for the Wyckoff positions 1a, 1b and 2c; only their site-symmetry groups are reduced. The special position 4b of $P4mm$ splits into 3 positions of $Cm$, one of which has also a reduced site symmetry (the general position 4b $(x,y,z)$).
EXERCISE: Monoclinic phase of the system PbZr$_{1-x}$Ti$_x$O$_3$

4.1 Solution

**Common subgroups of space groups $P4mm$ (99) and $R3m$ (160)**

Space group $G_1$: $P4mm$ (99) with $Z_H = 1$
Space group $G_2$: $R3m$ (160) with $Z_H = 3$

Maximum cell multiplication (for both branches): 1

NOTE: The program uses the default choice for the group settings.

<table>
<thead>
<tr>
<th>Common Subgroup H</th>
<th>Branch $G_1 &gt; H$</th>
<th>Branch $G_2 &gt; H$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$P_H$</td>
<td>$Z_H$</td>
</tr>
<tr>
<td>1</td>
<td>(2,1)</td>
<td>$Cm$</td>
</tr>
<tr>
<td>2</td>
<td>(3,2)</td>
<td>$P1$</td>
</tr>
</tbody>
</table>

**Transition paths in phase transitions not group-subgroup related**

Path number 1: $Cm(008)$ with $Z_H=2$

Symmetry conditions:

**Group-subgroup relations:**

- $G_1 > H_1$: $P4mm > Cm$ (index 4)
  - $P_1$: $a$-$b$,$a$-$b$,$c$
  - Transformation matrix:
    - $a_1 = \begin{bmatrix} -1 & 1 & 0 \\ -1 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$

- $G_2 > H_2$: $R3m > Cm$ (index 3)
  - $P_2$: $-1/3a+1/3b-2/3c$,$a$-$b$,$-1/3a+1/3b+1/3c$
  - Transformation matrix:
    - $a_2 = \begin{bmatrix} -1/3 & -1 & -1/3 \\ 1/3 & -1 & 1/3 \\ 0 & 1/3 & 0 \end{bmatrix}$

Note: $(a,b,c)_{H_1} = (a,b,c)_{G_1} P_1$; $(a,b,c)_{H_2} = (a,b,c)_{G_2} P_2$
Wyckoff positions splitting:

\[ P4mm > Cm \]

<table>
<thead>
<tr>
<th>#</th>
<th>AT</th>
<th>Coordinates in ( G_1 )</th>
<th>WP ( (G_1) )</th>
<th>WP ( (H_1) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>O1</td>
<td>(1/2,1/2,-0.10270)</td>
<td>1b(1/2,1/2,z)</td>
<td>2a(x,0,z)</td>
<td></td>
</tr>
<tr>
<td>O2</td>
<td>(1/2,0,0.37850)</td>
<td>2c(1/2,0,z)</td>
<td>4b(x,y,z)</td>
<td></td>
</tr>
<tr>
<td>Pb</td>
<td>(0,0,0)</td>
<td>1a(0,0,z)</td>
<td>2a(x,0,z)</td>
<td></td>
</tr>
<tr>
<td>Ti1</td>
<td>(1/2,1/2,0.45170)</td>
<td>1b(1/2,1/2,z)</td>
<td>2a(x,0,z)</td>
<td></td>
</tr>
</tbody>
</table>

\[ R3m > Cm \]

<table>
<thead>
<tr>
<th>#</th>
<th>AT</th>
<th>Coordinates in ( G_2 )</th>
<th>WP ( (G_2) )</th>
<th>WP ( (H_2) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>O1</td>
<td>(0.16200,0.32400,0.27100)</td>
<td>9b(x,-x,z)</td>
<td>4b(x,y,z)</td>
<td>2a(x,0,z)</td>
</tr>
<tr>
<td>Pb</td>
<td>(0,0,0)</td>
<td>3a(0,0,z)</td>
<td>2a(x,0,z)</td>
<td></td>
</tr>
<tr>
<td>Ti1</td>
<td>(0,0,0.45950)</td>
<td>3a(0,0,z)</td>
<td>2a(x,0,z)</td>
<td></td>
</tr>
</tbody>
</table>

Structural conditions:

Lattice deformation:

\[ \text{Unit cells (a,b,c,}\alpha,\beta,\gamma \text{) in } G_1 \text{ and } G_2 \]

\begin{align*}
&\text{In } G_1: 4.0460 4.0460 4.1394 90 90 90 \\
&\text{In } G_2: 5.7549 5.7549 7.1083 90 90 120
\end{align*}

\[ \text{Unit cells (a,b,c,}\alpha,\beta,\gamma \text{) in } H_1 \text{ and } H_2 \]

\begin{align*}
&\text{In } H_1: 5.7219 5.7219 4.1394 90 90 90 \\
&\text{In } H_2: 5.7876 5.7549 4.0813 90 90.45 90
\end{align*}

Strain tensor:

Degree of lattice distortion \( S = 0.0069 \)

\[
\text{Strain tensor } \eta = \begin{bmatrix}
-0.011197 & 0.000000 & 0.005594 \\
0.000000 & -0.005718 & 0.000000 \\
0.005584 & 0.000000 & 0.014337
\end{bmatrix}
\]

<table>
<thead>
<tr>
<th>Eigenvalues</th>
</tr>
</thead>
<tbody>
<tr>
<td>(-0.00571)</td>
</tr>
<tr>
<td>(-0.01235)</td>
</tr>
<tr>
<td>(0.015505)</td>
</tr>
</tbody>
</table>

Note: The degree of lattice distortion is described here by the \( S \) parameter, as the spontaneous strain (stress tensor) divided by 3. This \( S \) parameter must be smaller than the initial tolerance for the strain.
Mappings of the atoms:

Maximum distance $\Delta = 0.43508$

<table>
<thead>
<tr>
<th>Atom</th>
<th>Coordinates in $S_1$</th>
<th>Atom</th>
<th>Coordinates in $S_2$</th>
<th>Atomic Distances</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>$d_x$</td>
</tr>
<tr>
<td>Ti1[1]</td>
<td>(1/2,0,0.45170)</td>
<td>Ti1[1]</td>
<td>(0.54050,0,0.45950)</td>
<td>-0.04050</td>
</tr>
<tr>
<td>Ti1[2]</td>
<td>(0,1/2,0.45170)</td>
<td>Ti1[2]</td>
<td>(0.04050,1/2,0.45950)</td>
<td>-0.04050</td>
</tr>
<tr>
<td>O3[1]</td>
<td>(3/4,1/4,0.37850)</td>
<td>O3[2]</td>
<td>(0.81000,0.24300,0.43300)</td>
<td>-0.06000</td>
</tr>
<tr>
<td>O3[2]</td>
<td>(3/4,3/4,0.37850)</td>
<td>O3[1]</td>
<td>(0.81000,0.75700,0.43300)</td>
<td>-0.06000</td>
</tr>
<tr>
<td>O3[3]</td>
<td>(1/4,3/4,0.37850)</td>
<td>O3[4]</td>
<td>(0.31000,0.74300,0.43300)</td>
<td>-0.06000</td>
</tr>
<tr>
<td>O3[4]</td>
<td>(1/4,1/4,0.37850)</td>
<td>O3[3]</td>
<td>(0.31000,0.25700,0.43300)</td>
<td>-0.06000</td>
</tr>
<tr>
<td>O2[1]</td>
<td>(1/2,0,0.89730)</td>
<td>O2[1]</td>
<td>(0.56700,0,0.94700)</td>
<td>-1/15</td>
</tr>
<tr>
<td>O2[2]</td>
<td>(0,1/2,0.89730)</td>
<td>O2[2]</td>
<td>(1/15,1/2,0.94700)</td>
<td>-1/15</td>
</tr>
<tr>
<td>Pb4[1]</td>
<td>(0,0,0)</td>
<td>Pb4[1]</td>
<td>(0,0,0)</td>
<td>0</td>
</tr>
<tr>
<td>Pb4[2]</td>
<td>(1/2,1/2,0)</td>
<td>Pb4[2]</td>
<td>(1/2,1/2,0)</td>
<td>0</td>
</tr>
</tbody>
</table>

**Note:** In the table above are given the fractional coordinates of all atoms in the unit cell, of the initial structures in the ref specified distances $d_x$, $d_y$ and $d_z$ are relative distances, while $|d|$ is given in angstroms and is calculated with respect to