1 EXERCISE: Phase Transitions of $BaTiO_3$

1.1 Solution

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

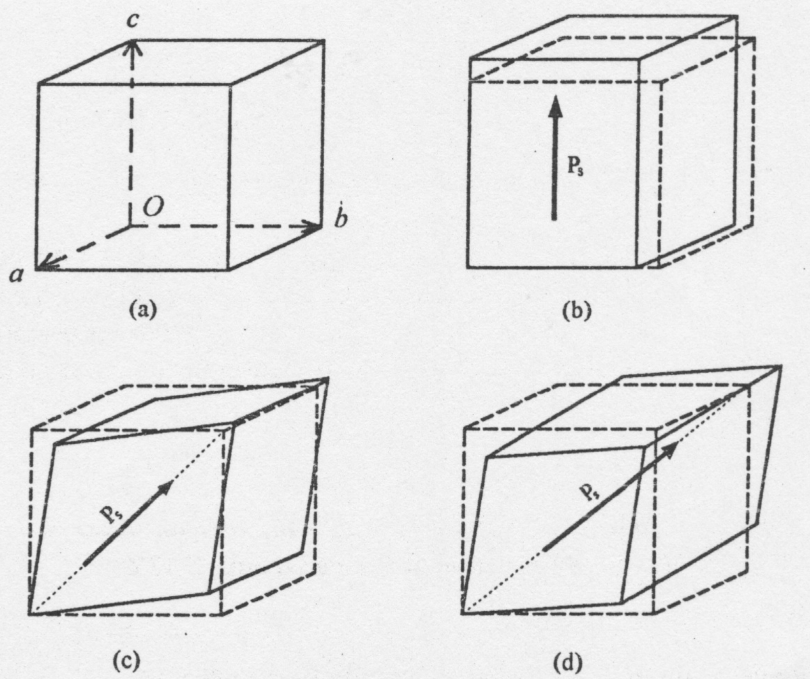

Fig. E9.1. Unit cells of the four phases of $BaTiO_3$. (a) cubic, stable above 120°C; (b) tetragonal, stable between 120°C and 5°C; (c) orthorhombic, stable between 5°C and -90°C; (d) rhombohedral, stable below -90°C. The dotted lines in (b), (c), and (d) delineate the original cubic cell. The heavy 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) Displacemente 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 **a',b',c'** two axes are chosen along face diagonals of the cubic cell (axes **a,b,c** and one along a cube edge; for instance, for the diagram (c):

a'=a, b'=b-c, c'=b+c (polar axis),

resulting in space group $Amm2$ (No. 38).

(iii) The subgroup indices are:

(b) $|\mathfrak{G}:\mathfrak{h}|=|Pm\bar{3}m:P4mm|=6$ threefold axes lost
(c) $|\mathfrak{G}:\mathfrak{h}|=|Pm\bar{3}m:Amm2|=12$ fourfold and threefold axes lost
(d) $|\mathfrak{G}:\mathfrak{h}|=|Pm\bar{3}m:R3m|=8$ 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, $2_z=4_z^2$, 4_z^1,4_z^{-1}=4_z^3,m_x,m_y,m_+ and m_-. The rotations are labelled as in the Fig.1 in order to describe the subgroups uniquely.

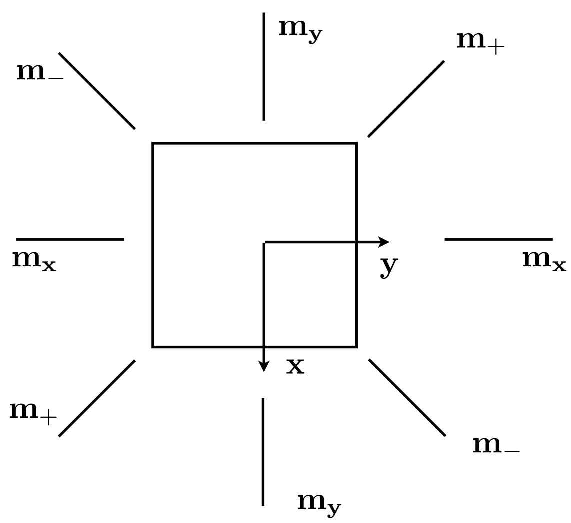

Fig.1. Symmetry group $4mm$=C_{4v} of the square

(i) Point group $4mm$ has three subgroups of index [2], *i.e.* order 4. Their Hermann-Mauguin symbols are 4_z,$\mathrm{m}_x\mathrm{m}_y2_z$ and $\mathrm{m}_+\mathrm{m}_-2_z$ where 2_z is contained in 4_z. The five subgroups of index [4], *i.e.* order 2, are 2_z,m_x,m_y,m_+ and 2_-.

(ii) Subgroups diagram of $4mm$ (Fig.2).

(iii) All three subgroups of index [2] (order 4) are normal, of the five subgroups of index [4], 2_z is normal (because it has no conjugates in $4mm$). The subgroups m_x and m_y, as well as m_+ and m_- each form a conjugate pair, because $\mathrm{m}_y = 4_z\mathrm{m}_x4_z^{-1}$ and $\mathrm{m}_+ = 4_z\mathrm{m}_-4_z^{-1}$ holds. (In subgroups diagrams conjugation is sometimes indicated by horizontal lines: m_x—m_y and m_+—m_-).

(iv) , (v) 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.* $P2_z\mathrm{m}1$. The lower symbol is the standard (short) Hermann-Mauguin symbol of the subgroups.

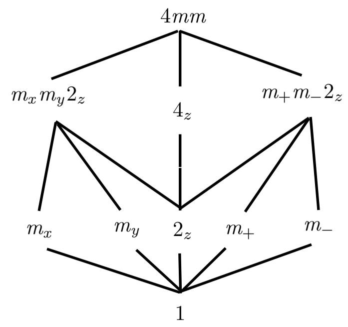

Fig. 2. Subgroup diagram of point group *4mm*

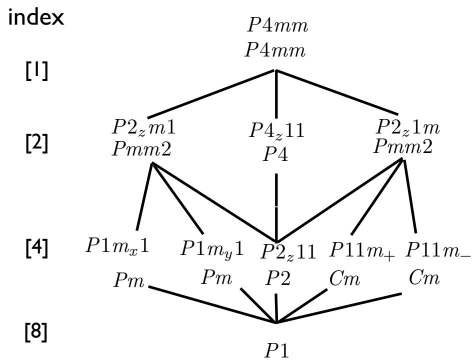

Fig. 3. *Translationengleiche* subgroups of space group *P4mm*

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 **a,b,c** of $P4mm$. Referred to **a',b',c'** the cell is C-centered, see Fig.4.

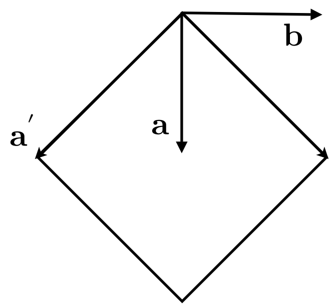

Fig. 4. Change of basis vectors: **a'=a-b**, **b'=a+b**

Changes of lattice-type symbols in subgroup relations are not uncommon. Another example are *translationengleiche* tetragonal subgroups of cubic F space groups: $Fm\bar{3}m \longrightarrow F4/m\bar{1}2/m \sim I4/mmm$, *etc.*, because there is no standard F for tetragonal spacegroups in IT A (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 $I4_1cd$ (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 (Mineralogy and Petrology, **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 $\mathcal{G}$, $\mathcal{S}_{\mathcal{G}}(X)$ and under its subgroup $\mathcal{H}$, $\mathcal{S}_{\mathcal{H}}(X)$, define the so-called reduction factors of the site symmetry : $R = \frac{|\mathcal{S}_{\mathcal{G}}(X)|}{|\mathcal{S}_{\mathcal{H}}(X)|}$. When the space-group symmetry is reduced from $\mathcal{G}$ to $\mathcal{H}$ and the orbit $\mathcal{O}_{\mathcal{G}}(X)$ of the point X in $\mathcal{G}$ splits into q orbits $\mathcal{O}_{\mathcal{H}}(X_j)$ 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 $\mathcal{O}_{\mathcal{G}}(X)$ 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 $\mathcal{H}$ are given by:

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

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

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

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:

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

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

$$2c\,\mathrm{2mm.}\,(1/2, 0, z) \rightarrow 4b\,1\,(x, y, z)$$

$$4d\,\mathrm{..m}\,(x, x, z) \rightarrow 4b\,1\,(x, y, z) \cup 2a\,\mathrm{m}\,(x, 0, z) \cup 2a\,\mathrm{m}\,(x, 0, z)$$

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)).

4 EXERCISE:Monoclinic phase of the system $PbZr_{1-x}Ti_xO_3$

4.1 Solution

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

Space group G_1:*P4mm* (99) with $Z_1 = 1$

Space group G_2:*R3m* (160) with $Z_2 = 3$

Maximum cell multiplication (for both branches): 1

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

Common Subgroup H							Branch $G_1 > H$			Branch $G_2 > H$		
N	#	LEVEL	HM Symbol	P_H	Z_H	ITA	i_1	it_1	ik_1	i_2	it_2	ik_2
1	◉	(2,1)	*Cm*	m	2	008	4	4	1	3	3	1
2	○	(3,2)	*P*1	1	1	001	8	8	1	6	6	1

Show Transition Paths

Transition paths in phase transitions not group-subgroup related

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

Symmetry conditions:

Group-subgroup relations:

#	Branch	(P,p)	Transformation matrix
$G_1 > H_1$	*P4mm* > *Cm* (index 4)	-a-b,a-b,c	$\begin{bmatrix} -1 & 1 & 0 \\ -1 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} 0 \\ 0 \\ 0 \end{bmatrix}$
$G_2 > H_2$	*R3m* > *Cm* (index 3)	-1/3a+1/3b-2/3c,-a-b,-1/3a+1/3b+1/3c	$\begin{bmatrix} -1/3 & -1 & -1/3 \\ 1/3 & -1 & 1/3 \\ -2/3 & 0 & 1/3 \end{bmatrix} \begin{bmatrix} 0 \\ 0 \\ 0 \end{bmatrix}$

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:

#	AT	Coordinates in G_1	WP (G_1)	WP (H_1)
P4mm > Cm	O1	(1/2,1/2,-0.10270)	1b(1/2,1/2,z)	2a(x,0,z)
	O2	(1/2,0,0.37850)	2c(1/2,0,z)	4b(x,y,z)
	Pb1	(0,0,0)	1a(0,0,z)	2a(x,0,z)
	Ti1	(1/2,1/2,0.45170)	1b(1/2,1/2,z)	2a(x,0,z)

#	AT	Coordinates in G_2	WP (G_2)	WP (H_2)
R3m > Cm	O1	(0.16200,0.32400,0.27100)	9b(x,-x,z)	4b(x,y,z) 2a(x,0,z)
	Pb1	(0,0,0)	3a(0,0,z)	2a(x,0,z)
	Ti1	(0,0,0.45950)	3a(0,0,z)	2a(x,0,z)

Structural conditions:

Lattice deformation:

Unit cells ($a,b,c,\alpha,\beta,\gamma$) in G_1 and G_2	Unit cells ($a,b,c,\alpha,\beta,\gamma$) in H_1 and H_2
In G_1: 4.0460 4.0460 4.1394 90 90 90 In G_2: 5.7549 5.7549 7.1083 90 90 120	In H_1: 5.7219 5.7219 4.1394 90 90 90 In H_2: 5.7876 5.7549 4.0813 90 90.45 90

Strain tensor:

Degree of lattice distortion S = 0.0069

Strain tensor η	Eigenvalues
[-0.011197 0.000000 0.005584] [0.000000 -0.005718 0.000000] [0.005584 0.000000 0.014337]	-0.00571 -0.01236 0.015505

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

Mappings of the atoms:

Maximum distance Δ = 0.43508

Atom	Coordinates in S_1	Atom	Coordinates in S_2	Atomic Distances			
				d_x	d_y	d_z	|d|
Ti1[1]	(1/2,0,0.45170)	Ti1[1]	(0.54050,0,0.45950)	- 0.04050	0	- 0.00780	0.23398
Ti1[2]	(0,1/2,0.45170)	Ti1[2]	(0.04050,1/2,0.45950)	- 0.04050	0	- 0.00780	0.23397
O3[1]	(3/4,1/4,0.37850)	O3[2]	(0.81000,0.24300,0.43300)	- 0.06000	+ 0.00700	- 0.05450	0.41275
O3[2]	(3/4,3/4,0.37850)	O3[1]	(0.81000,0.75700,0.43300)	- 0.06000	- 0.00700	- 0.05450	0.41275
O3[3]	(1/4,3/4,0.37850)	O3[4]	(0.31000,0.74300,0.43300)	- 0.06000	+ 0.00700	- 0.05450	0.41275
O3[4]	(1/4,1/4,0.37850)	O3[3]	(0.31000,0.25700,0.43300)	- 0.06000	- 0.00700	- 0.05450	0.41275
O2[1]	(1/2,0,0.89730)	O2[1]	(0.56700,0,0.94700)	-1/15	0	- 0.04970	0.43508
O2[2]	(0,1/2,0.89730)	O2[2]	(1/15,1/2,0.94700)	-1/15	0	- 0.04970	0.43508
Pb4[1]	(0,0,0)	Pb4[1]	(0,0,0)	0	0	0	0
Pb4[2]	(1/2,1/2,0)	Pb4[2]	(1/2,1/2,0)	0	0	0	0

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 amstrongs and is calculated with respect to