

Materials Science 142

Applications of Diffraction Techniques in Materials Science

Homework Assignment 3

Assigned: 1/25/12

Due: 2/01/12, 5pm

Reading 'International Tables'

Attached is a portion of the information in International Tables for Crystallography for space group $Pnma$ (#62). Provide the missing information. You may refer to the class handout on space group $Pmna$ (#53) for guidance, but do not use other references that may have the exact answers to the following questions.

- 1) Indicate the directions of the lattice parameters for the four projections. Recall the first three projections show the locations of the symmetry operations and the fourth the locations of an arbitrary object.
- 2) Draw in all of the symmetry operations in the third projection.
- 3) Using the first object already provided in the fourth projection, draw in the remaining objects within the unit cell. Indicate handedness and elevation using the proper notation.
- 4) Describe in words the 8 symmetry operations of this space group. For example, 'identity at all locations,' 'mirror operation in the ___ plane at ___.'
- 5) For the general Wyckoff position, x, y, z , provide a list of coordinates that indicates where the object will reside after operation on it by the symmetries of the space group. List these in the order corresponding to the list of symmetry operations shown. What is the multiplicity of the general position? What is the site symmetry of the general position?
- 6) Provide the reflection conditions for the general Wyckoff position (these correspond to the overall reflection conditions for this space group).
- 7) The special Wyckoff positions are at $x, \frac{1}{4}, z$; $0, 0, \frac{1}{2}$; and $0, 0, 0$. For each of these positions, provide a list of coordinates that indicates where the object will reside after operation on it by the symmetries of the space group. What are the multiplicities and site symmetries of each of these positions?
- 8) List any additional reflection conditions associated with these special positions.

Transformation of coordinates and space group settings

The space group and lattice constants of $BaCeO_3$ have been reported slightly differently by three different groups. Your task is to find out if these papers agree or disagree.

Source	space group	a (Å)	b(Å)	c(Å)
K. Takeuchi, <i>Solid State Ion.</i> , 2000	<i>Pmcn</i>	8.769(1)	6.229(1)	6.210(1)
L. Malavasi, <i>J. Appl. Phys.</i> , 2009	<i>Pnma</i>	6.21742(6)	8.77951(8)	6.23633(6)
A.J. Jacobson, <i>Acta Cryst. B</i> 1972	<i>Pbnm</i>	6.212(1)	6.235(1)	8.781(1)

The atomic coordinates have been given by Takeuchi (*Pmcn*) as

Atom	x	y	z
Ba	¼	-0.0039(4)	0.0173(3)
Ce	0	½	0
O(1)	¼	0.4273(3)	-0.0114(3)
O(2)	0.0388(1)	0.7244(2)	0.2768(2)

To find out if these sets of results are in agreement, you will need to determine the space group symbols for all of the six possible settings of space group *Pnma*.

- 1) Space group symbols for four of the possible settings of space group *Pnma* are given on the attached sheet. Indicate the relationship between the lattice constants for the standard setting, *Pnma*, and the transformed settings. For example, (abc) for space group *Pnma*, then (b \bar{a} c) for *Pmnb*. Write down the short hand notation for the four space groups.
- 2) Derive the complete space group symbols for the two missing settings. Provide the lattice constant relationship and the short hand notation for the settings.
- 3) Write down the transformation matrix that transforms space group *Pmcn* to space group *Pnma*. What is the determinant of this matrix? What does the determinant tell you about the relationship between the two cells?
- 4) Use the transformation matrix to determine the atomic coordinates in the standard setting, *Pnma*.
- 5) Use the transformation matrix to determine the hkl indices of the first six diffraction peaks in both the *Pmcn* and the *Pnma* settings.

X-ray Data Analysis:

1. Using the crystallographic data provided above for BaCeO₃ as reported by Takeuchi *et al.* and the XPert Plus software, generate the calculated diffraction pattern over the range 5 to 90° 2 θ . Use default values for atomic displacement parameters (or obtain these from the original paper) and instrument parameters. Note that the software appears to require that the data (atomic coordinates) be entered in the standard setting! Make sure you have done so.

2. A sample of BaCeO_3 has been prepared for X-ray diffraction data collection. Your TA will provide you guidance on how to load a sample into the diffractometer and operate the software for data collection. Select the 2θ data acquisition range based on the calculation above. Use default parameters for scan speed and 2θ resolution.
3. After the data acquisition is complete, run the search and match module to 'identify' your phase. Restrict your search such that Ba, Ce and O must be present in the compounds suggested by the software. This would correspond to a situation in which you tried to make a compound with these three elements but could not rule out the possibility of contamination by impurities.
4. Prepare a figure comparing the calculated pattern of part 1, with the measured pattern and showing the peak positions of the best match compound from the search-match step. Index the peaks. In the figure caption, provide the compound name, the space group (the setting must match the indexing), and the lattice constants (which must also match the setting and indexing).

Additional Problem:

Chapter 3: #5.

Attachments

Partial entry for space group $Pnma$

Complete entry for space group $P6_3/mmc$ (for textbook problem).

$Pnma$

D_{2h}^{16}

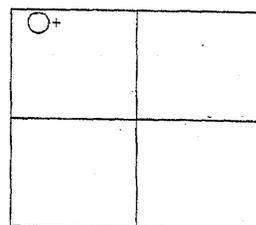
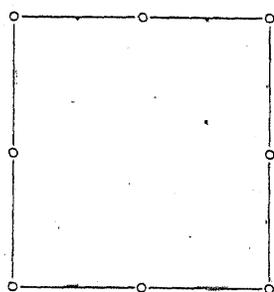
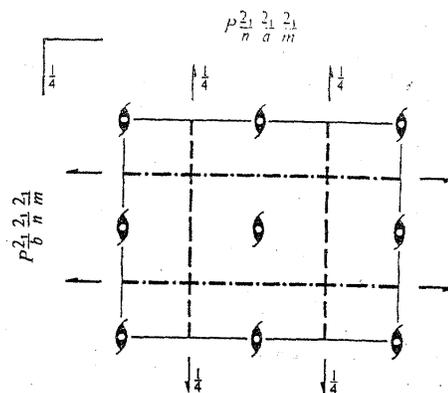
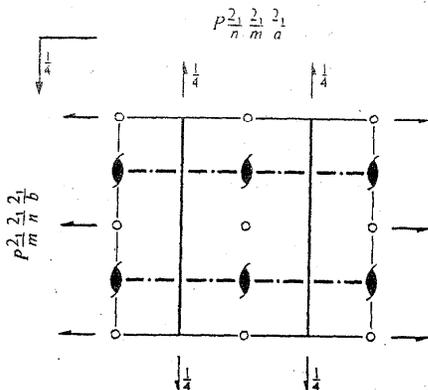
mmm

Orthorhombic

No. 62

$P2_1/n 2_1/m 2_1/a$

Patterson symmetry $Pmmm$



Origin at $\bar{1}$ on 12,1

Asymmetric unit $0 \leq x \leq \frac{1}{2}$; $0 \leq y \leq \frac{1}{2}$; $0 \leq z \leq 1$

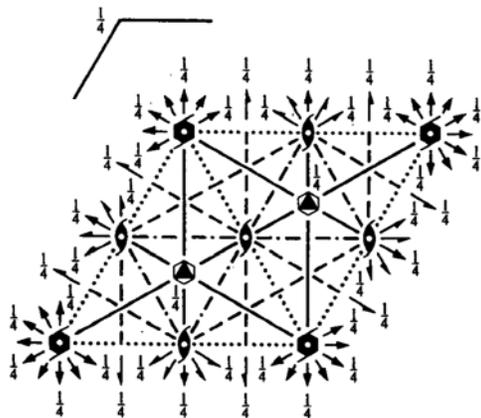
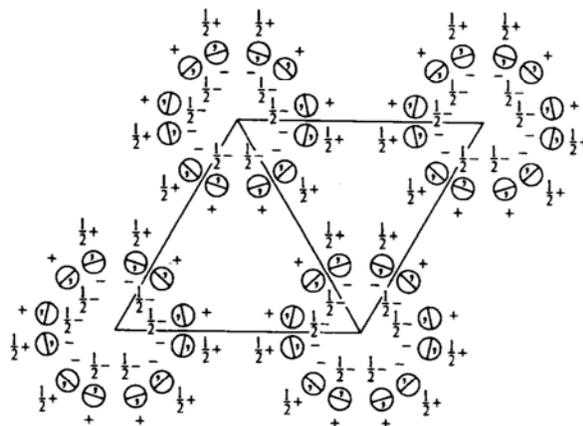
Symmetry operations

- | | | | | | | | |
|---------------|--------------------------|-------------------|--------------------------|---------|--------------------------|------------------------------------|-------------------|
| (1) 1 | (2) $2(0,0,\frac{1}{2})$ | $\frac{1}{2},0,z$ | (3) $2(0,\frac{1}{2},0)$ | $0,y,0$ | (4) $2(\frac{1}{2},0,0)$ | $x,\frac{1}{2},\frac{1}{2}$ | |
| (5) $\bar{1}$ | $0,0,0$ | (6) a | $x,y,\frac{1}{2}$ | (7) m | $x,\frac{1}{2},z$ | (8) $n(0,\frac{1}{2},\frac{1}{2})$ | $\frac{1}{2},y,z$ |

$P6_3/mmc$ D_{6h}^4 $6/mmm$

Hexagonal

No. 194

 $P6_3/m2/m2/c$ Patterson symmetry $P6/mmm$ For $\bar{1}$ and $\bar{6}$ see $P6_3/m$ (No. 176)Origin at centre ($\bar{3}m1$) at $\bar{3}2/mc$ Asymmetric unit $0 \leq x \leq \frac{1}{2}$; $0 \leq y \leq \frac{1}{2}$; $0 \leq z \leq \frac{1}{2}$; $x \leq 2y$; $y \leq \min(1-x, 2x)$

Vertices $0,0,0$ $\frac{1}{2},\frac{1}{2},0$ $\frac{1}{2},\frac{1}{2},0$
 $0,0,\frac{1}{2}$ $\frac{1}{2},\frac{1}{2},\frac{1}{2}$ $\frac{1}{2},\frac{1}{2},\frac{1}{2}$

Symmetry operations

- | | | |
|----------------------------------|--|--|
| (1) 1 | (2) 3^+ $0,0,z$ | (3) 3^- $0,0,z$ |
| (4) $2(0,0,\frac{1}{2})$ $0,0,z$ | (5) $6^-(0,0,\frac{1}{2})$ $0,0,z$ | (6) $6^+(0,0,\frac{1}{2})$ $0,0,z$ |
| (7) 2 $x,x,0$ | (8) 2 $x,0,0$ | (9) 2 $0,y,0$ |
| (10) 2 $x,\bar{x},\frac{1}{2}$ | (11) 2 $x,2x,\frac{1}{2}$ | (12) 2 $2x,x,\frac{1}{2}$ |
| (13) $\bar{1}$ $0,0,0$ | (14) $\bar{3}^+$ $0,0,z$; $0,0,0$ | (15) $\bar{3}^-$ $0,0,z$; $0,0,0$ |
| (16) m $x,y,\frac{1}{2}$ | (17) 6^- $0,0,z$; $0,0,\frac{1}{2}$ | (18) 6^+ $0,0,z$; $0,0,\frac{1}{2}$ |
| (19) m x,\bar{x},z | (20) m $x,2x,z$ | (21) m $2x,x,z$ |
| (22) c x,x,z | (23) c $x,0,z$ | (24) c $0,y,z$ |

Maximal non-isomorphic subgroups

- I**
- | | |
|------------------------------|---|
| [2] $P6_322$ | 1; 2; 3; 4; 5; 6; 7; 8; 9; 10; 11; 12 |
| [2] $P6_3/m11(P6_3/m)$ | 1; 2; 3; 4; 5; 6; 13; 14; 15; 16; 17; 18 |
| [2] $P6_3mc$ | 1; 2; 3; 4; 5; 6; 19; 20; 21; 22; 23; 24 |
| [2] $P\bar{3}m1$ | 1; 2; 3; 7; 8; 9; 13; 14; 15; 19; 20; 21 |
| [2] $P\bar{3}1c$ | 1; 2; 3; 10; 11; 12; 13; 14; 15; 22; 23; 24 |
| [2] $P\bar{6}m2$ | 1; 2; 3; 10; 11; 12; 16; 17; 18; 19; 20; 21 |
| [2] $P\bar{6}2c$ | 1; 2; 3; 7; 8; 9; 16; 17; 18; 22; 23; 24 |
| [3] $Pm\bar{m}c(Cm\bar{c}m)$ | 1; 4; 7; 10; 13; 16; 19; 22 |
| [3] $Pm\bar{m}c(Cm\bar{c}m)$ | 1; 4; 8; 11; 13; 16; 20; 23 |
| [3] $Pm\bar{m}c(Cm\bar{c}m)$ | 1; 4; 9; 12; 13; 16; 21; 24 |

IIa none**IIb** [3] $H6_3/mmc(a'=3a, b'=3b)(P6_3/mcm)$

Maximal isomorphic subgroups of lowest index

IIc [3] $P6_3/mmc(c'=3c)$; [4] $P6_3/mmc(a'=2a, b'=2b)$

Minimal non-isomorphic supergroups

I none

Generators selected (1); $t(1,0,0)$; $t(0,1,0)$; $t(0,0,1)$; (2); (4); (7); (13)

Positions

Multiplicity,
Wyckoff letter,
Site symmetry

Coordinates

Reflection conditions

24	<i>l</i>	1	(1) x, y, z	(2) $\bar{y}, x-y, z$	(3) $\bar{x}+y, \bar{x}, z$
			(4) $\bar{x}, \bar{y}, z+\frac{1}{2}$	(5) $y, \bar{x}+y, z+\frac{1}{2}$	(6) $x-y, x, z+\frac{1}{2}$
			(7) y, x, \bar{z}	(8) $x-y, \bar{y}, \bar{z}$	(9) $\bar{x}, \bar{x}+y, \bar{z}$
			(10) $\bar{y}, \bar{x}, \bar{z}+\frac{1}{2}$	(11) $\bar{x}+y, y, \bar{z}+\frac{1}{2}$	(12) $x, x-y, \bar{z}+\frac{1}{2}$
			(13) $\bar{x}, \bar{y}, \bar{z}$	(14) $y, \bar{x}+y, \bar{z}$	(15) $x-y, x, \bar{z}$
			(16) $x, y, \bar{z}+\frac{1}{2}$	(17) $\bar{y}, x-y, \bar{z}+\frac{1}{2}$	(18) $\bar{x}+y, \bar{x}, \bar{z}+\frac{1}{2}$
			(19) \bar{y}, \bar{x}, z	(20) $\bar{x}+y, y, z$	(21) $x, x-y, z$
			(22) $y, x, z+\frac{1}{2}$	(23) $x-y, \bar{y}, z+\frac{1}{2}$	(24) $\bar{x}, \bar{x}+y, z+\frac{1}{2}$

General:

$hh\bar{2}hl: l = 2n$
 $000l: l = 2n$

Special: as above, plus

12	<i>k</i>	$.m.$	$x, 2x, z$	$2\bar{x}, \bar{x}, z$	x, \bar{x}, z	$\bar{x}, 2\bar{x}, z+\frac{1}{2}$
			$2x, x, z+\frac{1}{2}$	$\bar{x}, x, z+\frac{1}{2}$	$2x, x, \bar{z}$	$\bar{x}, 2\bar{x}, \bar{z}$
			\bar{x}, x, \bar{z}	$2\bar{x}, \bar{x}, \bar{z}+\frac{1}{2}$	$x, 2x, \bar{z}+\frac{1}{2}$	$x, \bar{x}, \bar{z}+\frac{1}{2}$

no extra conditions

12	<i>j</i>	$m..$	$x, y, \frac{1}{2}$	$\bar{y}, x-y, \frac{1}{2}$	$\bar{x}+y, \bar{x}, \frac{1}{2}$	$\bar{x}, \bar{y}, \frac{1}{2}$	$y, \bar{x}+y, \frac{1}{2}$	$x-y, x, \frac{1}{2}$
			$y, x, \frac{1}{2}$	$x-y, \bar{y}, \frac{1}{2}$	$\bar{x}, \bar{x}+y, \frac{1}{2}$	$\bar{y}, \bar{x}, \frac{1}{2}$	$\bar{x}+y, y, \frac{1}{2}$	$x, x-y, \frac{1}{2}$

no extra conditions

12	<i>i</i>	$.2.$	$x, 0, 0$	$0, x, 0$	$\bar{x}, \bar{x}, 0$	$\bar{x}, 0, \frac{1}{2}$	$0, \bar{x}, \frac{1}{2}$	$x, x, \frac{1}{2}$
			$\bar{x}, 0, 0$	$0, \bar{x}, 0$	$x, x, 0$	$x, 0, \frac{1}{2}$	$0, x, \frac{1}{2}$	$\bar{x}, \bar{x}, \frac{1}{2}$

$hkil: l = 2n$

6	<i>h</i>	$mm2$	$x, 2x, \frac{1}{2}$	$2\bar{x}, \bar{x}, \frac{1}{2}$	$x, \bar{x}, \frac{1}{2}$	$\bar{x}, 2\bar{x}, \frac{1}{2}$	$2x, x, \frac{1}{2}$	$\bar{x}, x, \frac{1}{2}$
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no extra conditions

6	<i>g</i>	$.2/m.$	$\frac{1}{2}, 0, 0$	$0, \frac{1}{2}, 0$	$\frac{1}{2}, \frac{1}{2}, 0$	$\frac{1}{2}, 0, \frac{1}{2}$	$0, \frac{1}{2}, \frac{1}{2}$	$\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$
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$hkil: l = 2n$

4	<i>f</i>	$3m.$	$\frac{1}{2}, \frac{1}{2}, z$	$\frac{1}{2}, \frac{1}{2}, z+\frac{1}{2}$	$\frac{1}{2}, \frac{1}{2}, \bar{z}$	$\frac{1}{2}, \frac{1}{2}, \bar{z}+\frac{1}{2}$
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$hkil: l = 2n$
or $h-k = 3n+1$
or $h-k = 3n+2$

4	<i>e</i>	$3m.$	$0, 0, z$	$0, 0, z+\frac{1}{2}$	$0, 0, \bar{z}$	$0, 0, \bar{z}+\frac{1}{2}$
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$hkil: l = 2n$

2	<i>d</i>	$\bar{6}m2$	$\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$	$\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$	}
2	<i>c</i>	$\bar{6}m2$	$\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$	$\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$	

$hkil: l = 2n$
or $h-k = 3n+1$
or $h-k = 3n+2$

2	<i>b</i>	$\bar{6}m2$	$0, 0, \frac{1}{2}$	$0, 0, \frac{1}{2}$
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$hkil: l = 2n$

2	<i>a</i>	$\bar{3}m.$	$0, 0, 0$	$0, 0, \frac{1}{2}$
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$hkil: l = 2n$

Symmetry of special projections

Along [001] $p6mm$

$a' = a$ $b' = b$

Origin at $0, 0, z$

Along [100] $p2gm$

$a' = \frac{1}{2}(a+2b)$ $b' = c$

Origin at $x, 0, 0$

Along [210] $p2mm$

$a' = \frac{1}{2}b$ $b' = \frac{1}{2}c$

Origin at $x, \frac{1}{2}x, 0$

(Continued on preceding page)