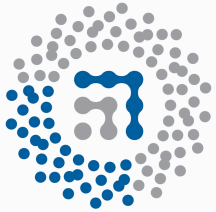


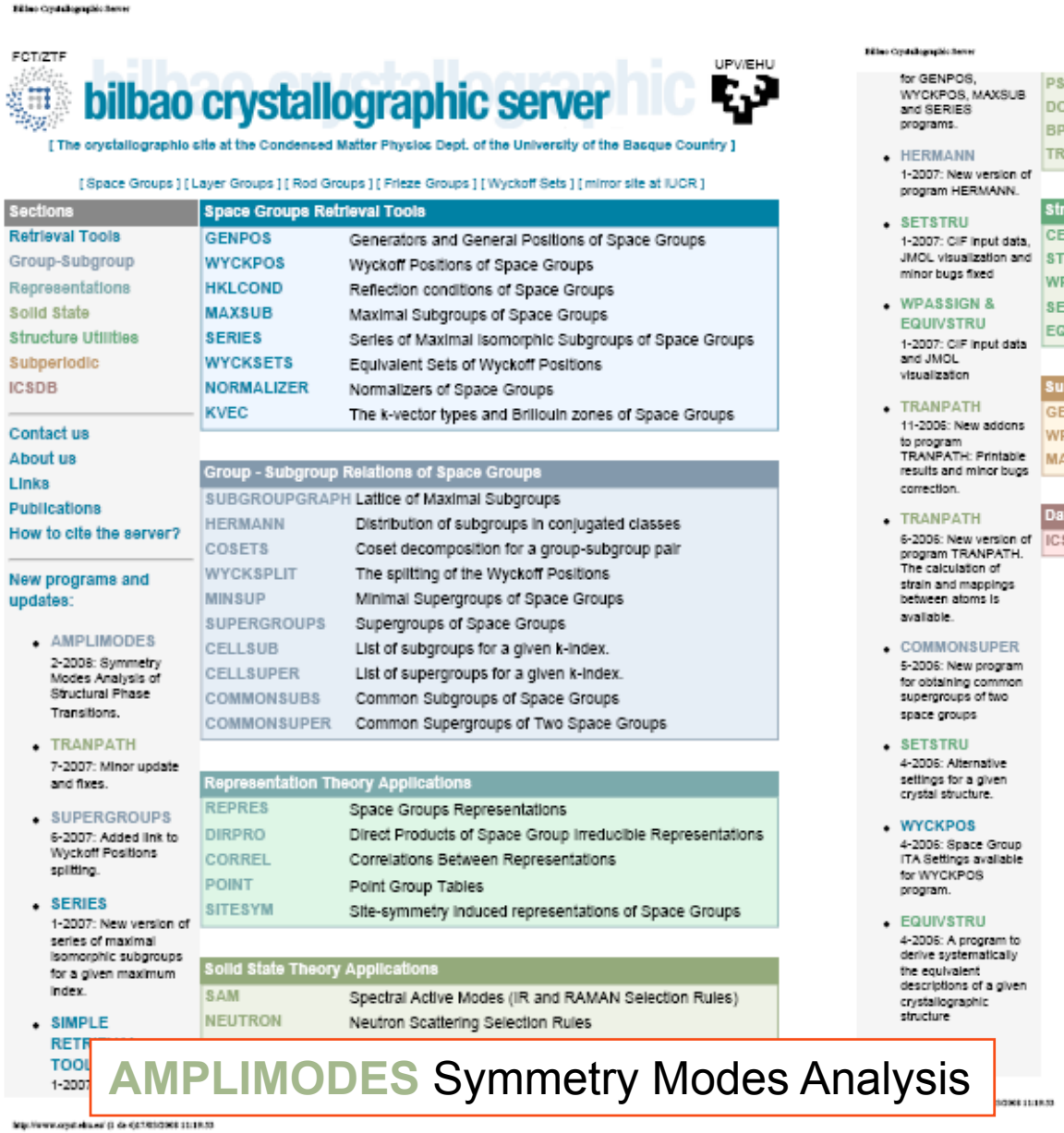
ZTF-FCT
Zientzia eta Teknologia Fakultatea
Facultad de Ciencia y Tecnología

eman ta zabal zazu
Universidad del País Vasco
Euskal Herriko Unibertsitatea

Symmetry mode analysis in the Bilbao Crystallographic Server:

The program AMPLIMODES

http://www.cryst.ehu.es



FCT/ZTF

UPV/EHU

bilbao crystallographic server

[The crystallographic site at the Condensed Matter Physics Dept. of the University of the Basque Country]

[Space Groups] [Layer Groups] [Rod Groups] [Frieze Groups] [Wyckoff Sets] [mirror site at IUCR]

Sections

- Retrieval Tools
- Group-Subgroup
- Representations
- Solid State
- Structure Utilities
- Subperiodic
- ICSDB

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- Publications
- How to cite the server?

New programs and updates:

- **AMPLIMODES** 2-2008: Symmetry Modes Analysis of Structural Phase Transitions.
- **TRANPATH** 7-2007: Minor update and fixes.
- **SUPERGROUPS** 6-2007: Added link to Wyckoff Positions splitting.
- **SERIES** 1-2007: New version of series of maximal isomorphic subgroups for a given maximum index.
- **SIMPLE RETR... TOOL...** 1-2007

Space Groups Retrieval Tools

GENPOS	Generators and General Positions of Space Groups
WYCKPOS	Wyckoff Positions of Space Groups
HKLCOND	Reflection conditions of Space Groups
MAXSUB	Maximal Subgroups of Space Groups
SERIES	Series of Maximal Isomorphic Subgroups of Space Groups
WYCKSETS	Equivalent Sets of Wyckoff Positions
NORMALIZER	Normalizers of Space Groups
KVEC	The k-vector types and Brillouin zones of Space Groups

Group - Subgroup Relations of Space Groups

SUBGROUPGRAPH	Lattice of Maximal Subgroups
HERMANN	Distribution of subgroups in conjugated classes
COSETS	Coset decomposition for a group-subgroup pair
WYCKSPLIT	The splitting of the Wyckoff Positions
MINSUP	Minimal Supergroups of Space Groups
SUPERGROUPS	Supergroups of Space Groups
CELLSUB	List of subgroups for a given k-index.
CELLSUPER	List of supergroups for a given k-index.
COMMONSUBS	Common Subgroups of Space Groups
COMMONSUPER	Common Supergroups of Two Space Groups

Representation Theory Applications

REPRES	Space Groups Representations
DIRPRO	Direct Products of Space Group Irreducible Representations
CORREL	Correlations Between Representations
POINT	Point Group Tables
SITESYM	Site-symmetry Induced representations of Space Groups

Solid State Theory Applications

SAM	Spectral Active Modes (IR and RAMAN Selection Rules)
NEUTRON	Neutron Scattering Selection Rules

for GENPOS, WYCKPOS, MAXSUB and SERIES programs.

- **HERMANN** 1-2007: New version of program HERMANN.
- **SETSTRU** 1-2007: CIF input data, JMOL visualization and minor bugs fixed
- **WPASSIGN & EQUIVSTRU** 1-2007: CIF input data and JMOL visualization
- **TRANPATH** 11-2006: New addons to program TRANPATH: Printable results and minor bugs correction.
- **TRANPATH** 6-2006: New version of program TRANPATH. The calculation of strain and mappings between atoms is available.
- **COMMONSUPER** 5-2006: New program for obtaining common supergroups of two space groups
- **SETSTRU** 4-2006: Alternative settings for a given crystal structure.
- **WYCKPOS** 4-2006: Space Group ITA Settings available for WYCKPOS program.
- **EQUIVSTRU** 4-2006: A program to derive systematically the equivalent descriptions of a given crystallographic structure

PSEUDO	Pseudosymmetry Search in a Structure
DOPE	Degree of Pseudosymmetry Estimation
BPLOT	Pseudosymmetry Search with KPLOT
TRANPATH	Transition Paths (Group not subgroup relations)

Structure Utilities

CELLTRAN	Transform Unit Cells
STRAIN	Strain Tensor Calculation
WPASSIGN	Assignment of Wyckoff Positions
SETSTRU	Alternative Settings for a given Crystal Structure
EQUIVSTRU	Equivalent Descriptions for a given Crystal Structure

Subperiodic Groups: Layer, Rod and Frieze Groups Retrieval Tools

GENPOS	Generators and General Positions of Subperiodic Groups
WPOS	Wyckoff Positions of Subperiodic Groups
MAXSUB	Maximal Subgroups of Subperiodic Groups

Databases

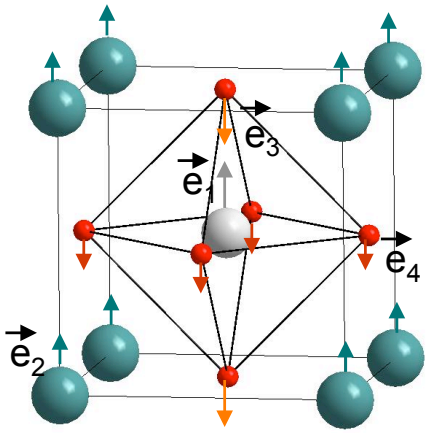
ICSDB	Inconmensurate Crystal Structure Database

AMPLIMODES Symmetry Modes Analysis

Modes in the statics of low-symmetry distorted phases:

Distorted Structure = High-symmetry Struct + "frozen" modes

distortion mode = Amplitude x polarization vector



Description of a "mode":

$\vec{u}(\text{atoms}) = Q\,\vec{e}$

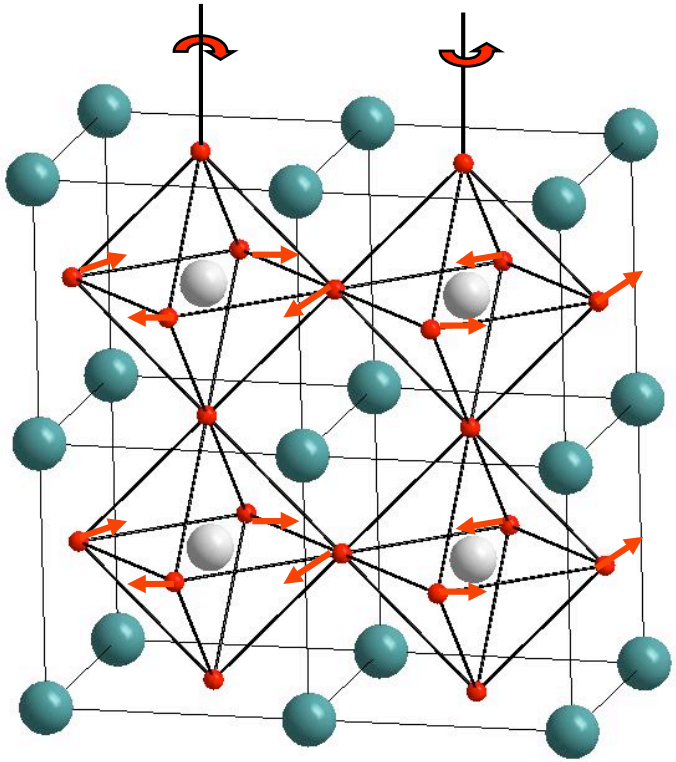
amplitude | polarization vector

$\mathbf{e} = (\vec{e}_1, \vec{e}_2, \vec{e}_3, \vec{e}_4)$

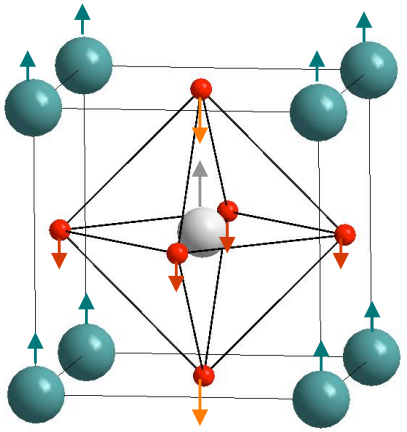
normalization: $|\vec{e}_1|^2 + |\vec{e}_2|^2 + |\vec{e}_3|^2 + 2\,|\vec{e}_4|^2 = 1$
(within a unit cell)

AMPLIMODES calculates the amplitudes and polarization vectors of all distortion modes with different symmetries (irreps) frozen in a distorted structure.

We can compare the amplitudes of different frozen distortion modes:



$Q_2 \vec{e}_2$

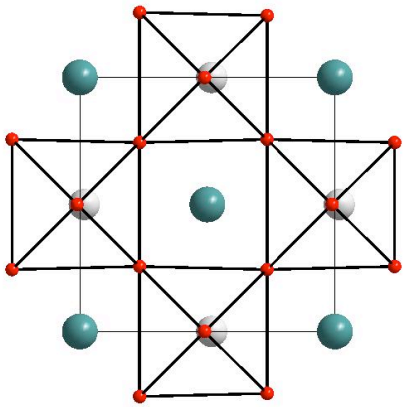


$Q_1 \vec{e}_1$

Q_1 and Q_2 have the same dimensions and their values can be compared

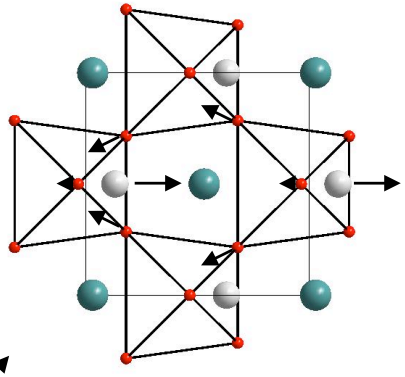
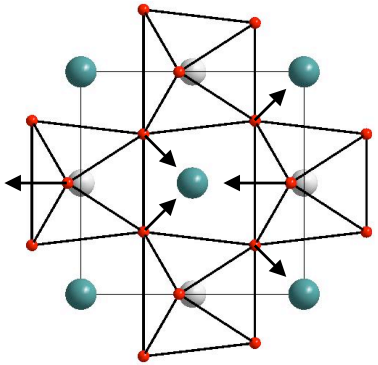
The orthorhombic Amm2 structure of $BaTiO_3$

(Kwei et al. (1993) neutron-powder 190 K)



max. atomic displ. : 0.13 Å

Mode decomposition of distortion:

Q_{GM4-} x  + Q_{GM5-} x 

GM4- mode

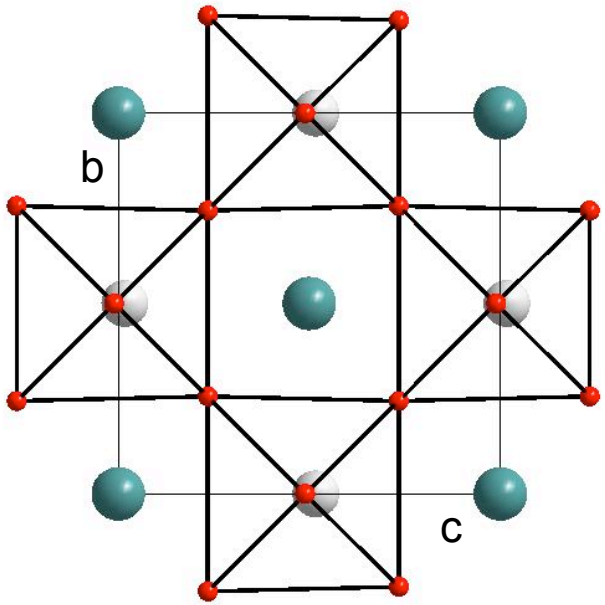
GM5- mode

polar ferroelectric mode

$Q_{GM4-} >> Q_{GM5-}$

Example of input of AMPLIMODES:

Amm2 phase of $BaTiO_3$



High symmetry structure

Pm-3m

```
221
4.006 4.006 4.006 90 90 90
3
Ba      1    1a      0.0 0.0 0
Ti      1    1b      0.5 0.5 0.5
O       1    3c      0.5 0.0 0.5
```

Low symmetry structure

Amm2

```
38
3.9828 5.6745 5.6916 90 90 90
4
Ba      1    2a      0.0 0.0 0.0
Ti      1    2b      0.5 0.0 0.5170
O       1    2a      0.0 0.0 0.4890
O       2    4e      0.5 0.2561 0.2343
```

4 parameters

Transformation matrix

Transf.

```
[      0      1      1 ]  [      0]
[      0     -1      1 ]  [      0]
[      1      0      0 ]  [      0]
```

Example of output of AMPLIMODES:

Transformed high symmetry structure in the subgroup basis

```
038
4.006000 5.665339 5.665339 90.000000 90.000000 90.000000
4
Ba      1       2a      0.000000        0.000000        0.000000
Ti      1       2b      0.500000        0.000000        0.500000
O       1       4e      0.500000        0.250000        0.250000
O       1_2     2a      0.000000        0.000000        0.500000
```

Atom pairings and distances

Atom Mappings					
WP		Atom	Coordinates in S_1	Atom	Coordinates in S_2
2a	(0,0,z)	Ba1	(0,0,0)	Ba1	(0,0,0)
2b	(1/2,0,z)	Ti1	(1/2,0,1/2)	Ti1	(1/2,0,0.51700)
4e	(1/2,y,z)	O1	(1/2,1/4,1/4)	O2	(1/2,0.25610,0.23430)
2a	(0,0,z)	O1_2	(0,0,1/2)	O1	(0,0,0.48900)

WP		Atom	Atomic Distances			
			u_x	u_y	u_z	|d|
2a	(0,0,z)	Ba1	0.0000	0.0000	0.0000	0.0000
2b	(1/2,0,z)	Ti1	0.0000	0.0000	0.0170	0.0963
4e	(1/2,y,z)	O1	0.0000	0.0061	-0.0157	0.0954
2a	(0,0,z)	O1_2	0.0000	0.0000	-0.0110	0.0623

NOTE: d_x, d_y and d_z are given in relative units. |d| is the absolute distance given in Å

Maximum atomic displacement in the distortion, Δ: 0.0963 Å
Total distortion amplitude: 0.1771 Å

After origin shift

Relative origin shift to eliminate a global displacement: (0.00000, 0.00000, -0.00508)

Atom Mappings					
WP		Atom	Coordinates in S_1	Atom	Coordinates in S_2
2a	(0,0,z)	Ba1	(0,0,0)	Ba1	(0,0,0.00508)
2b	(1/2,0,z)	Ti1	(1/2,0,1/2)	Ti1	(1/2,0,0.52208)
4e	(1/2,y,z)	O1	(1/2,1/4,1/4)	O2	(1/2,0.25610,0.23938)
2a	(0,0,z)	O1_2	(0,0,1/2)	O1	(0,0,0.49408)

WP		Atom	Atomic Distances			
			u_x	u_y	u_z	|d|
2a	(0,0,z)	Ba1	0.0000	0.0000	0.0051	0.0288
2b	(1/2,0,z)	Ti1	0.0000	0.0000	0.0221	0.1251
4e	(1/2,y,z)	O1	0.0000	0.0061	-0.0106	0.0694
2a	(0,0,z)	O1_2	0.0000	0.0000	-0.0059	0.0335

NOTE: d_x, d_y and d_z are given in relative units. |d| is the absolute distance given in Å

Maximum atomic displacement in the distortion, Δ: 0.1251 Å
Total distortion amplitude: 0.1650 Å

Symmetry Modes Summary

Atoms	WP	Modes
O1	3*c*	**GM4-(2) GM5-(1)**
Ti1	1*b*	**GM4-(1)**
Ba1	1*a*	**GM4-(1)**

Note: The primary mode is written in bold letters

Summary of Amplitudes

K-vector	Irrep	Direction	Isotropy Subgroup	Dimension	Amplitude (Å)
(0,0,0)	GM4-	(a,a,0)	Amm2 (38)	4	0.1649
(0,0,0)	GM5-	(0,a,-a)	Amm2 (38)	1	0.0056

Global distortion: 0.1650 Å

Example of output of AMPLIMODES:

Normalized Symmetry modes

The modes are normalized to the low symmetry unit c
cell and are given as relative displacements in this cell.

Irrep GM4-

GM4- Mode Ba1 1

Atom	δx	δy	δz
Ba1	0.000000	0.000000	0.176512

GM4- Mode Ti1 1

Atom	δx	δy	δz
Ti1	0.000000	0.000000	0.176512

GM4- Mode O1 1

Atom	δx	δy	δz
O1	0.000000	0.062406	0.062406
O1_2	0.000000	0.000000	0.124813

GM4- Mode O1 2

Atom	δx	δy	δz
O1	0.000000	-0.088256	0.088256
O1_2	0.000000	0.000000	0.000000

basis for this 4dim vector

Irrep GM5-

GM5- Mode O1 1

Atom	δx	δy	δz
O1	0.000000	-0.062406	-0.062406
O1_2	0.000000	0.000000	0.124813

K-vector: GM = (0,0,0)

Irrep: GM4-

Direction: (a,a,0)

Isotropy Subgroup: 38 Amm2 C2v-14

Transformation matrix:

```
[     0     1     1 ] [     0]
[     0    -1     1 ] [     0]
[     1     0     0 ] [     0]
```

amplitude of the GM4- distortion

The amplitude of this distortion is:
A_{GM4-} = 0.1649 Å

Normalized polarization vector: (in terms of the amplitudes of the (normalized)

Ba1 1	Ti1 1	O1 1	O1 2
0.1745	0.7585	-0.2536	-0.5744

NOTE: A second number next to the label counts the different symmetry modes that

Normalized polarization vector expressed as displacements (in cell relative un
Ångström)

Atom	δx	δy	δz
Ba1	0.0000	0.0000	0.0308
Ti1	0.0000	0.0000	0.1339
O1	0.0000	0.0349	-0.0665
O1_2	0.0000	0.0000	-0.0317

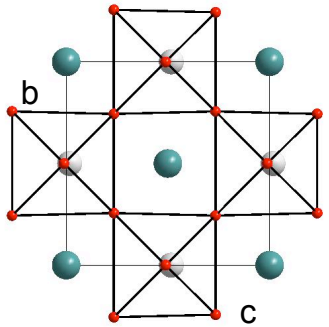
polarization vector in two forms

crystallographic form

Virtual structure with only this symmetry component of the distortion frozen.

The orthorhombic Amm2 structure of $BaTiO_3$

(Kwei et al. (1993) neutron-powder 190 K)



Perovskite in Amm2 setting

	δx	δy	δz
Ba1	0.0	0.0	0.0
Ti1	0.5	0.0	0.5
O1	0.5	0.25	0.25
O12	0.0	0.0	0.5

+

polarization vector GM4-

	δx	δy	δz
Ba1	0.0	0.0000	0.0308
Ti1	0.0	0.0000	0.1339
O1	0.0	0.0349	-0.0665
O12	0.0	0.0000	-0.0317

+ Q_{GM4-}

polarization vector GM5-

	δx	δy	δz
Ba1	0.0	0.0000	0.0000
Ti1	0.0	0.0000	0.0000
O1	0.0	0.0624	0.0624
O12	0.0	0.0000	-0.1248

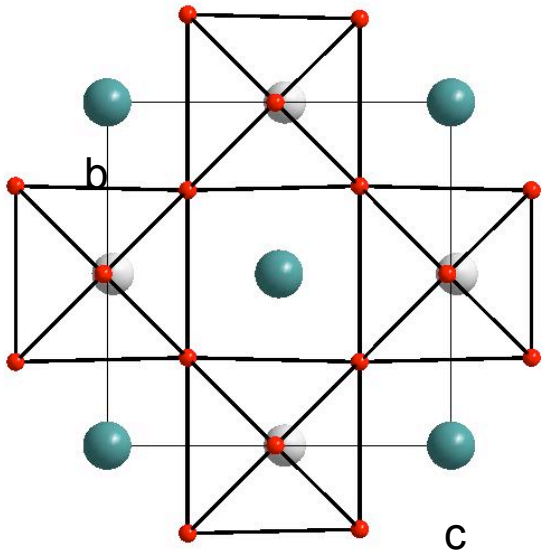
+ Q_{GM5-}

Q_{GM4-} = 0.165 Å

Q_{GM5-} = 0.006 Å

The orthorhombic Amm2 structure of $BaTiO_3$

(Kwei et al. (1993) neutron-powder 190 K)



Amm2

Ba	1	2a	0.0	0.0	0.0
Ti	1	2b	0.5	0.0	0.5170
O	1	2a	0.0	0.0	0.4690
O	2	4e	0.5	0.2561	0.2343

4 parameters

The orthorhombic Amm2 structure of $BaTiO_3$

Orthorhombic Distortion

$Q_{T1u} >> Q_{T2u}$

Polar (ferroelectric) mode

T_{1u}

Q_{T1u} x

	δx	δy	δz
Ba1	0.0	0.0000	0.0308
Ti1	0.0	0.0000	0.1339
O1	0.0	0.0349	-0.0665
O12	0.0	0.0000	-0.0317

Symmetry T_{1u} :

$\delta y_{O1} + \delta z_{O1} - \delta z_{O12} = 0$

zero global translation :

$2\delta z_{Ba1} + 2\delta z_{Ti11} + 4\delta z_{O12} + 2\delta z_{O12} = 0$

normalization

3 parameters

+ Q_{T2u} x

Non-polar mode

T_{2u}

	δx	δy	δz
Ba1	0.0	0.0000	0.0000
Ti1	0.0	0.0000	0.0000
O1	0.0	0.0624	0.0624
O12	0.0	0.0000	-0.1248

Symmetry T_{1u} :

$\delta y_{O1} + \delta z_{O1} + \delta z_{O12} = 0$

$\delta y_{O1} = \delta z_{O1}$

normalization

1 parameter

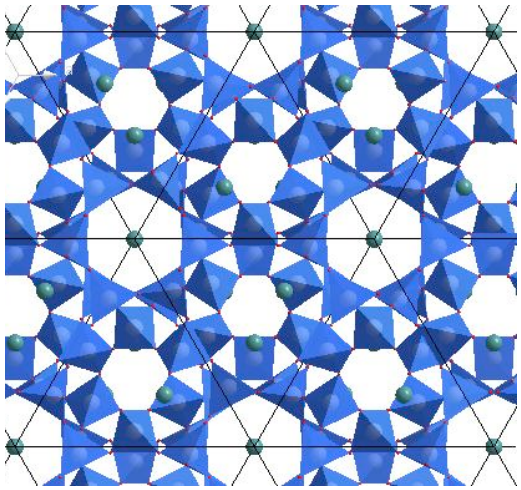
Leucite

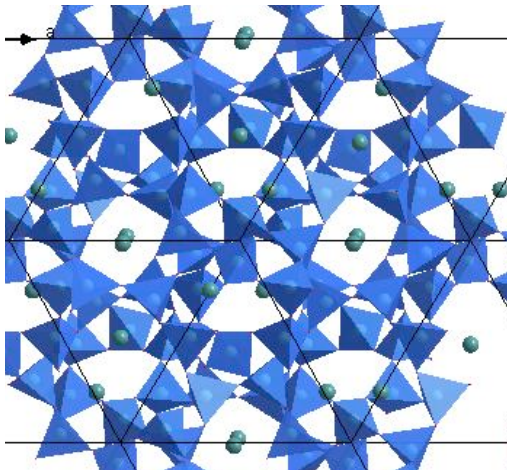
$KAlSi_2O_6$

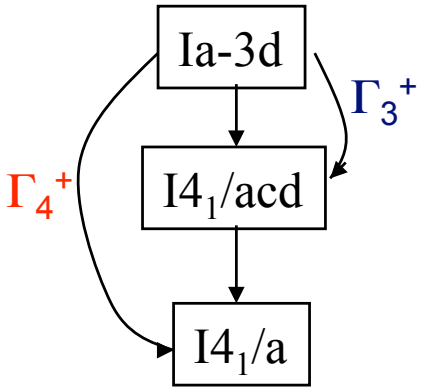
$I4_1/a$

Palmer et. (Amer. Miner. 82 (1997) 16

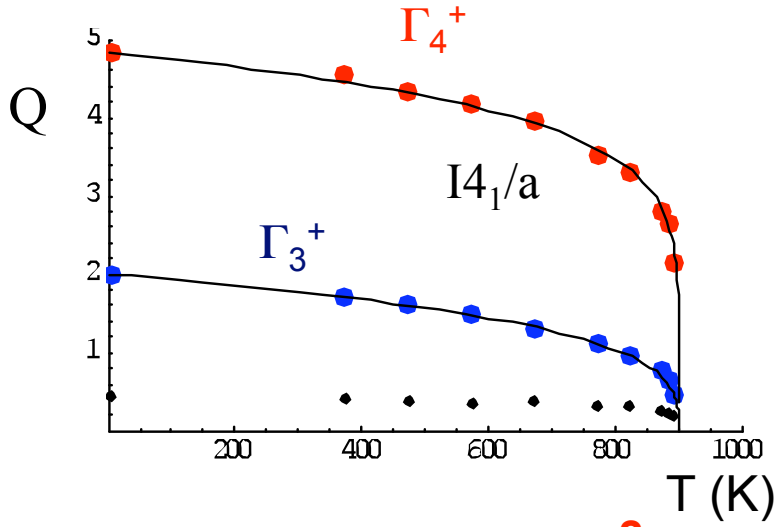
max. atomic displ. : 1.04Å







DISTORTION AMPLITUDES VS. TEMPERATURE:

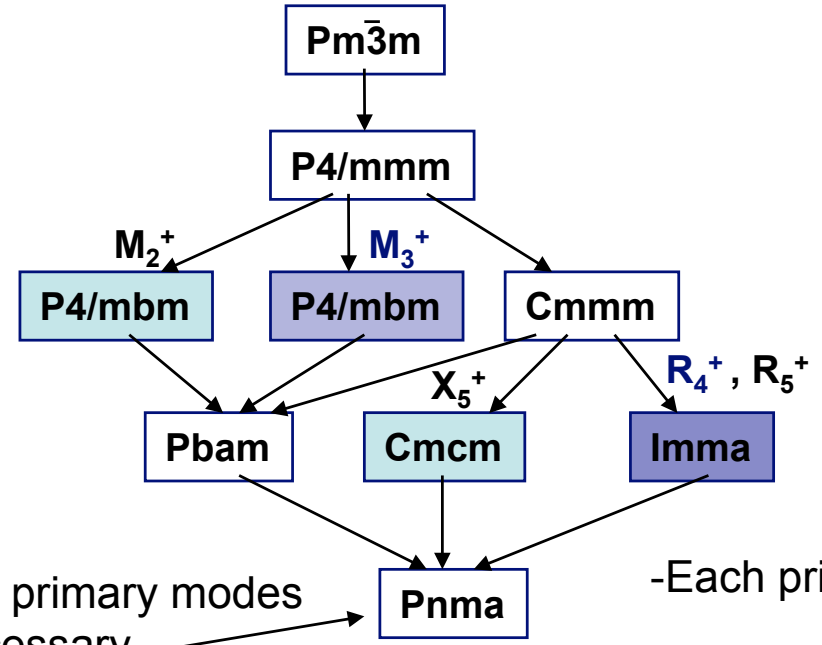


Induced effect : $Q_{\Gamma 3+} = \alpha\, Q^2_{\Gamma 4+}$

Sequence of transitions in $SrZrO_3$

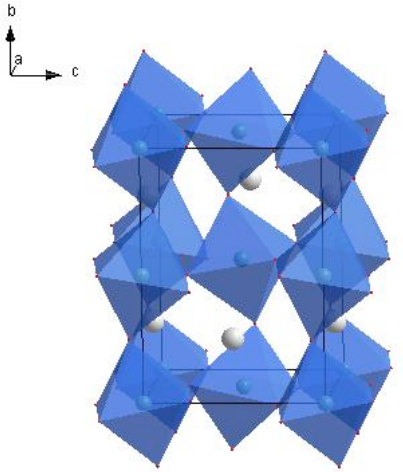
20 C

(Howard et al. 2000 & data from B. Kennedy)



two primary modes necessary

Pnma



Pnma

-Each primary mode is a different instability mechanism

- each primary mode condenses in general at different temperatures : two phase transitions

Q_{M2+} = 0.007 Å

Q_{M3+} = 0.794 Å

Q_{X5+} = 0.338 Å

Q_{R4+} = 1.185 Å

Q_{R5+} = 0.069 Å

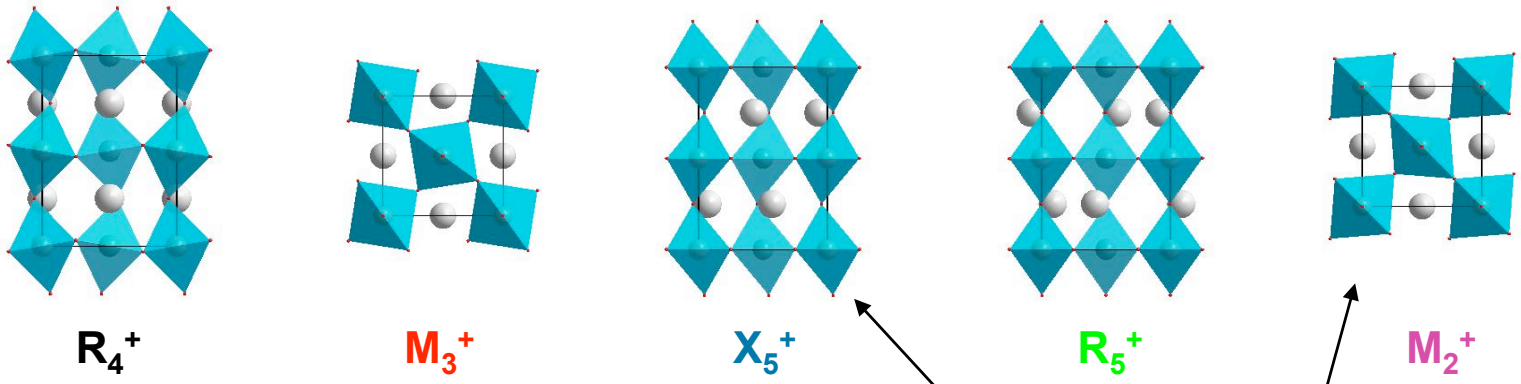
→ Pnma

Expected transition sequence:

T > →

Pnma (M_3^+, R_4^+) → Imma (R_4^+) → Pm$\bar{3}$m

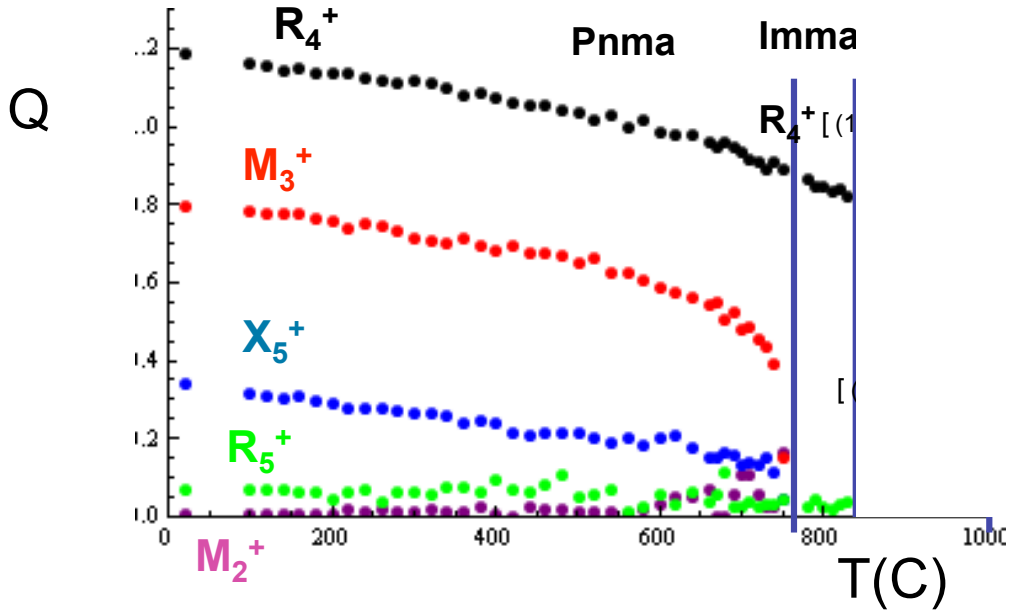
Sequence of transitions in $SrZrO_3$



R_4^+	M_3^+	X_5^+	R_5^+	M_2^+
1.18 Å	0.79 Å	0.338 Å	0.07 Å	0.007 Å

They deform the octahedra.
X_5^+ has significant amplitude

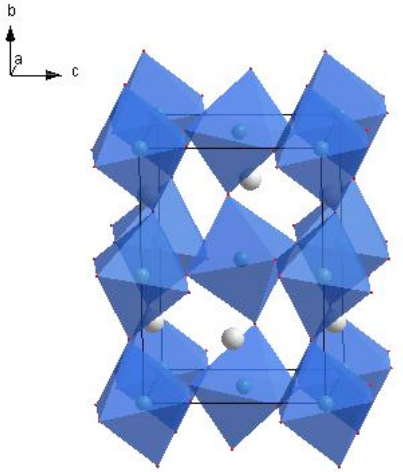
(Howard et al. 2000 & data from B. Kennedy)

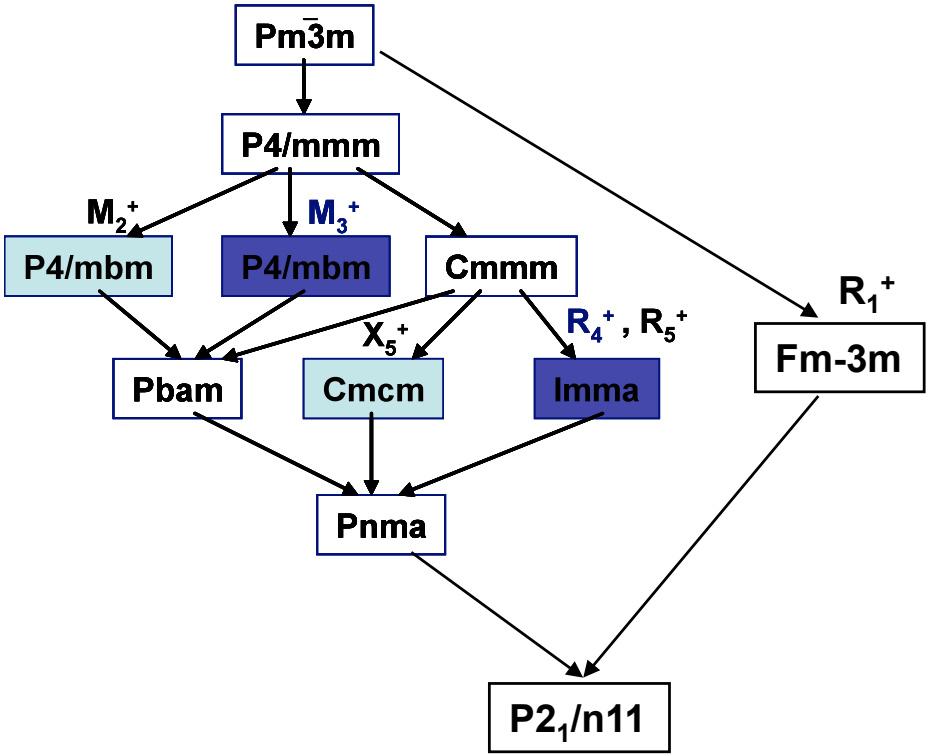


$PrNiO_3$

$P2_1/n11(P2_1/c)$ instead of Pnma ?

Medarde et al. PRL (2007)



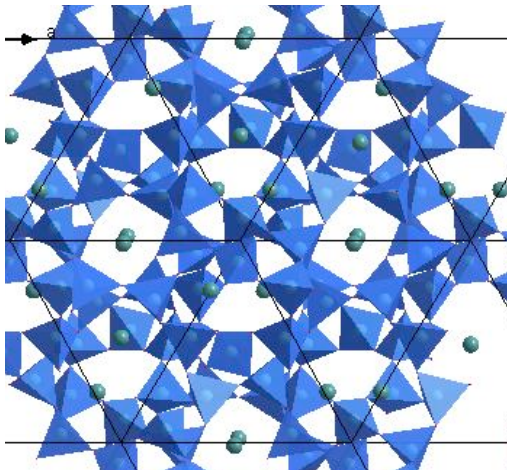


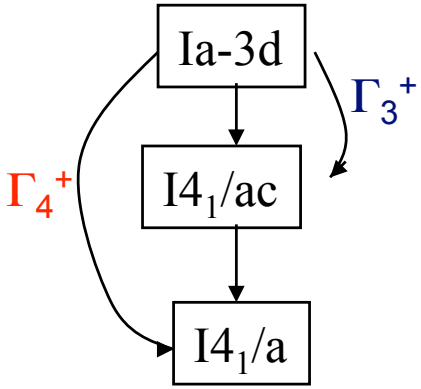
Amplitudes		SrZrO3	PrNiO3
R4+	(Imma)	1.19	1.09
M3+	(P4/mbm)	0.79	0.69
X5+	(Cmcm)	0.34	0.36
R5+		0.07 (Imma)	0.06 (C2/m)
M2+	(P4/mbm)	0.01	0.00
R1+ ??	(Fm-3m)	-	**0.09**
R3+	(I4/mmm)	-	0.01
M5+	(Pmna)	-	0.00

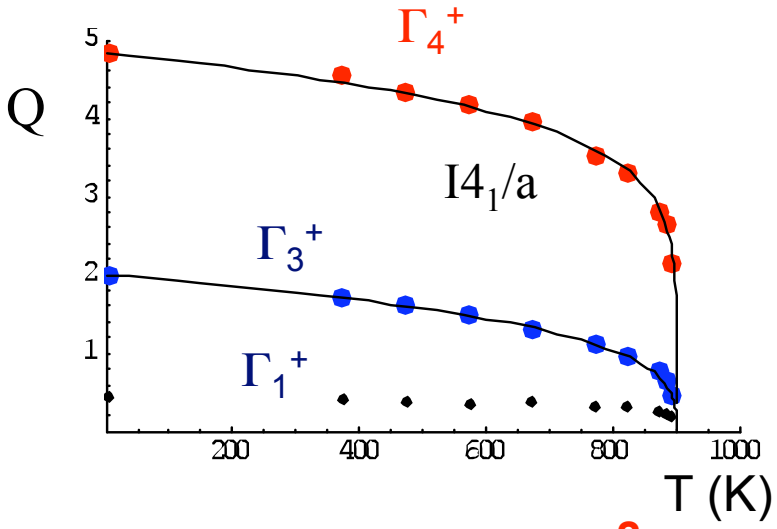
Polarization vectors in Leucite

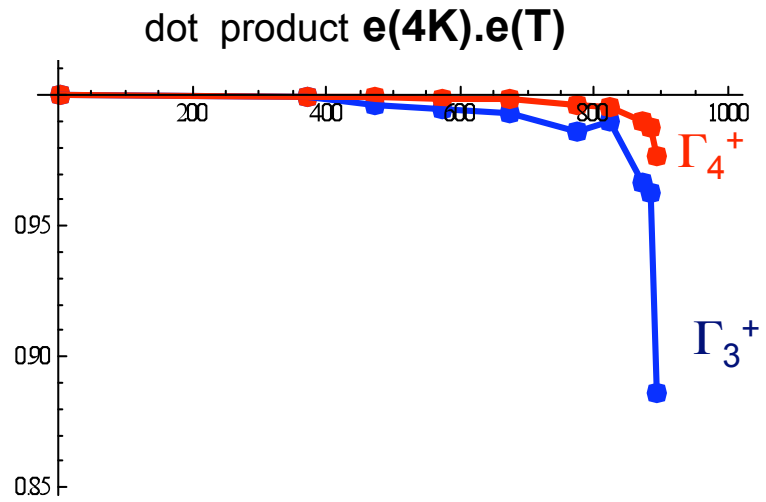
$I4_1/a$ Palmer et. (Amer. Miner. 82 (1997) 16

$KAlSi_2O_6$





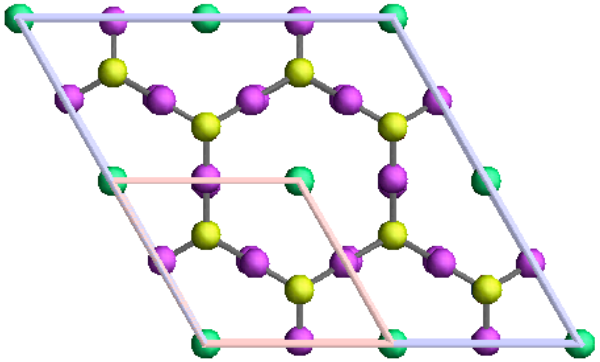




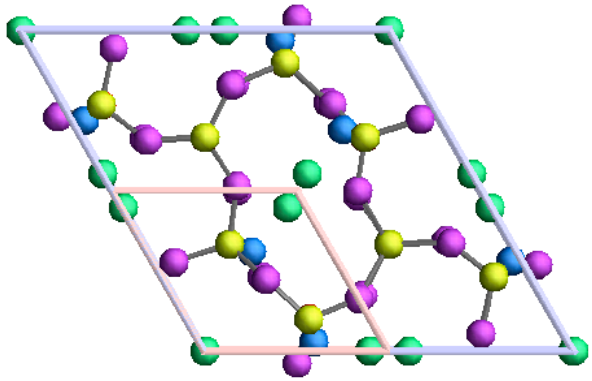
Induced effect : $Q_{\Gamma 3+} = \alpha\, Q^2_{\Gamma 4+}$

Polymorphism: nephelines $Na_{8-r}Al_{8-r}Si_{8+r}O_4$ $(r \approx 0)$

Virtual arystotype: $P6_3mc$



$P6_3$



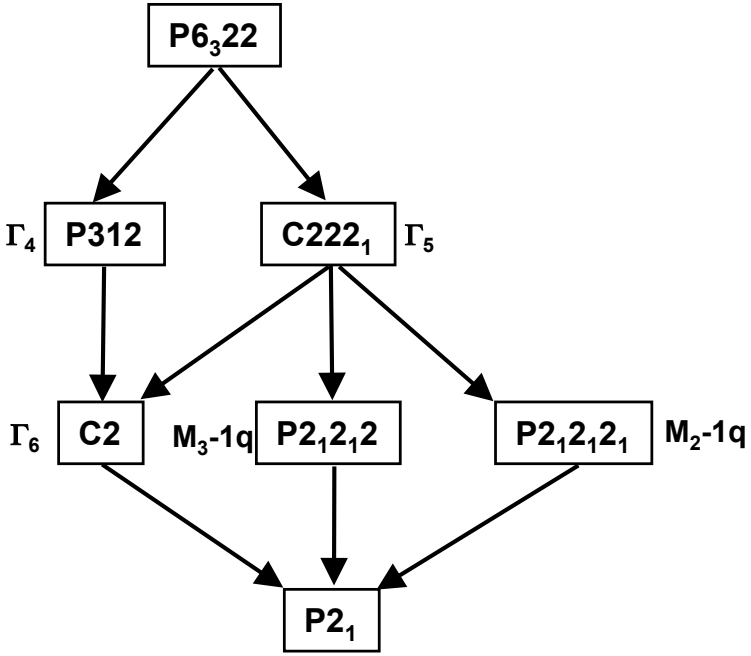
	Ampl. (Å)	Dim.
GM2 (P63):	0.09	1
M1(P63mc,2x2x1):	0.39	13
M2(P63,2x2x1):	**2.89**	**8**

(max. atomic displ. : 1.34Å)

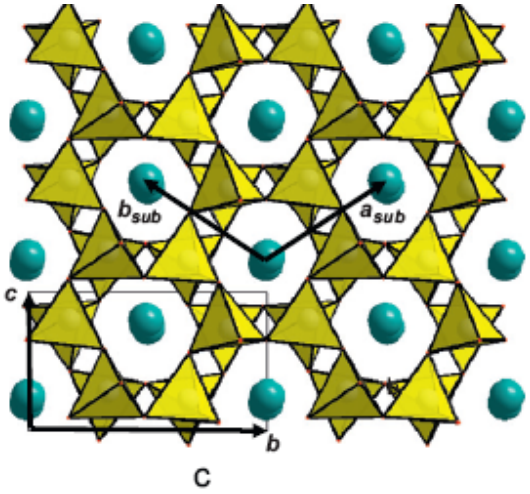
Mode decomposition vs. ab-initio calculations

$SrAl_2O_4$

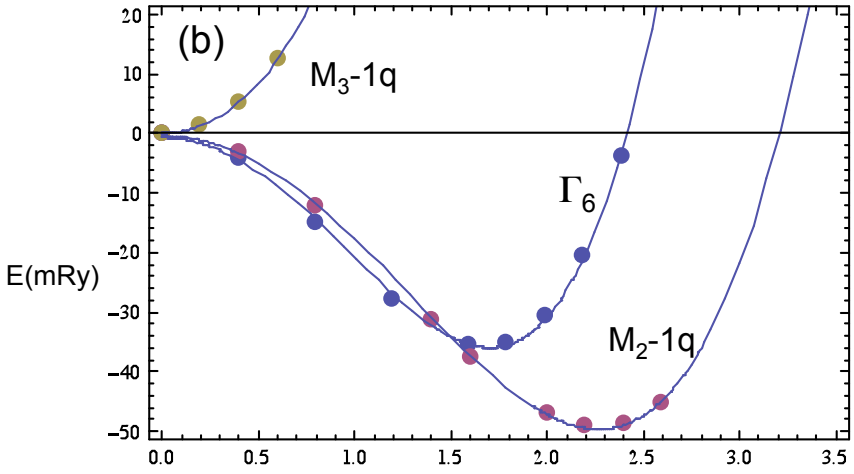
$P6_322 \longrightarrow P2_1$



(Larsson et al. 2008)

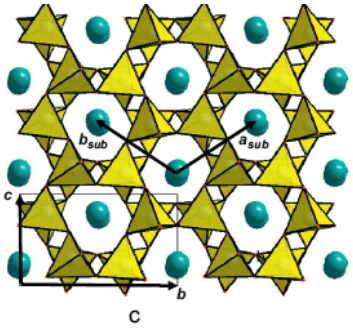


two different displacive instabilities:



$SrAl_2O_4$

Comparison of mode decomposition of experimental and ab-initio structures



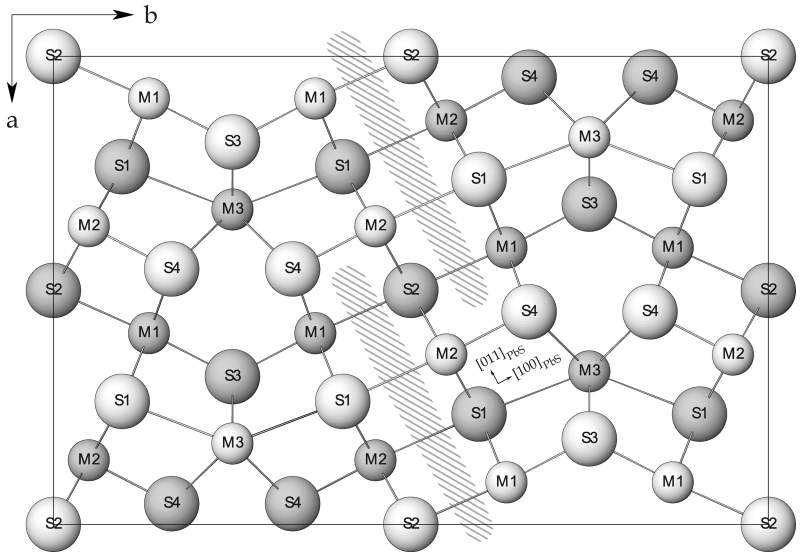
Amplitudes and dot products of polarization vectors :

irrep	M_2-1q		Γ_6		M_3-1q		Γ_5		Γ_4	
dim.	12		7		11		7		3	
	Amp.	prod.	Amp.	prod.	Amp.	prod.	Amp.	prod.	Amp.	prod.
Exp. Struct.	1.70		1.39		0.57		0.32		0.02	
ab-initio	1.81	0.998	1.35	0.9997	0.57	0.997	0.24	0.96	0.03	0.63

Mode decomposition in "collapse" high pressure phase transitions

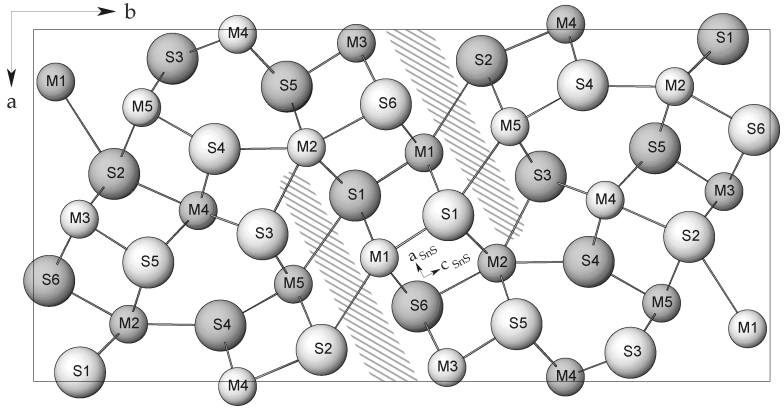
Lillianite: $Pb_3Bi_2S_6$

Olsen et al., Inorg. Chem. 2008,47 6/56



0 GPa

Bbmm



4.7 GPa

Pbnm

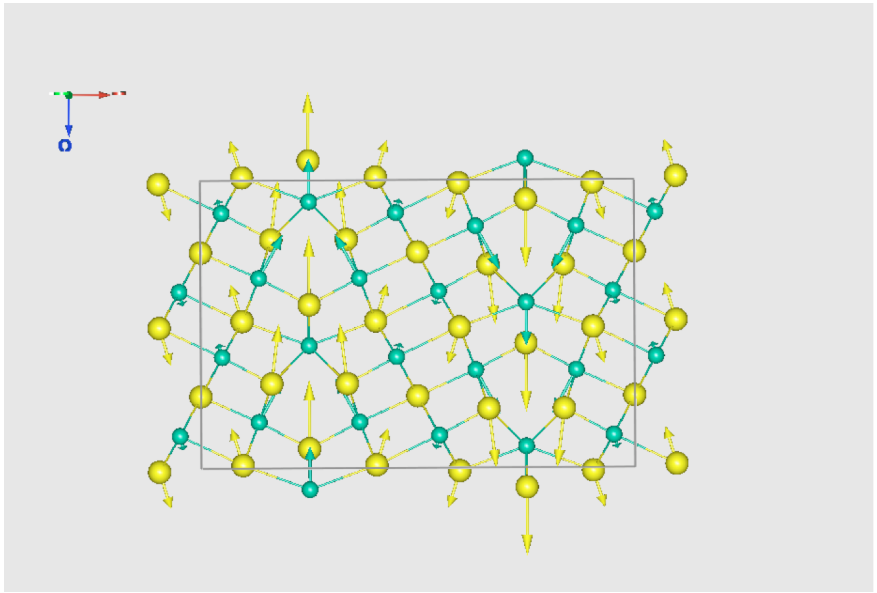
Mode decomposition in "collapse" high pressure phase transitions

Lillianite: $Pb_3Bi_2S_6$

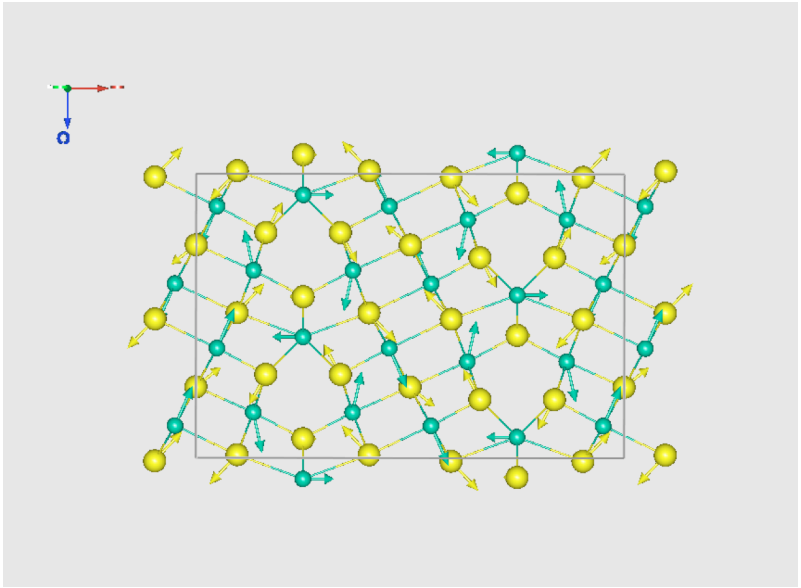
Mode decomposition of High-pressure phase:

Active irrep distortion but also large fully symmetric distortion

Fully symmetric distortion: irrep GM1



symmetry breaking distortion: active irrep Y2-



Symmetry-mode coordinates in the structure refinement, instead of the individual atomic coordinates:

AMPLIMODES → **FullProf** (Juan Rodriguez-Carvajal)

(for powder or single crystal diffraction refinement)

One expects:

- a natural hierarchy of parameters
- less correlations with atomic (thermal) displacement parameters
- better control of the refinement

Example of PCR file for **FullProf** corresponding to the compound $LaMnO_3$

```
! Polarisation Vectors of Symmetry Modes for each atom
V_MODES    12
! Nm Atm      Irrep          Vx          Vy          Vz          Coeff
   1  O1        R4+        0.000000    0.000000    0.031721     1.000000
   1  O2        R4+        0.063442    0.000000    0.000000     1.000000
   2  La        R5+       -0.089721    0.000000    0.000000     1.000000
   3  O1        R5+        0.000000    0.000000   -0.031721     1.000000
  . . . . .    . . . . . .
   7  O2        M3+        0.000000    0.000000    0.000000     1.000000
! Amplitudes of Symmetry Modes
A_MODES    7      1 1 1 1 1 1 1
Q1_R4+          -1.189680   181.0000
Q2_R5+          -0.086467   191.0000
Q3_R5+           0.018171   201.0000
Q4_X5+          -0.546082   211.0000
Q5_X5+          -0.139910   221.0000
Q6_M2+           0.355652   231.0000
Q7_M3+           0.901264   241.0000
!-------> Profile Parameters for Pattern #  1
!  Scale          Shape1       Bov      Str1     Str2     Str3  Strain-Model
 0.86919E-01    0.00000    0.00000   0.0000   0.0000   0.0000         0
. . . . . . . . .
```

Symbols of the Irreducible representations

Polarisation vectors components

Keyword, # of modes, output for FST

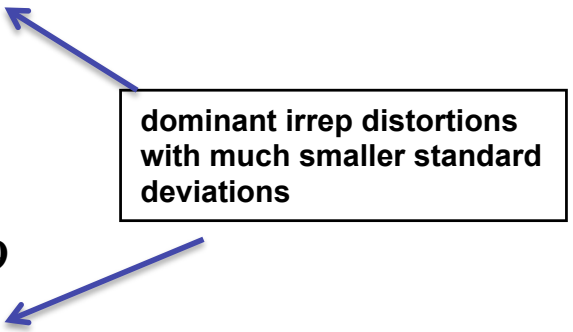
Names of amplitudes, values and refinement codes (allowing constraints)

Example of direct refinement of mode amplitudes with FullProf:

Symmetry Mode amplitudes have very different amplitudes and their standard deviations may differ in orders of magnitude

=> Amplitudes of symmetry modes ==>

Name	Value	Sigma
Q1_GM1+	-0.274537	0.008771
Q2_GM3+	0.037956	0.031615
Q3_GM4+	0.804386	0.007905
Q4_GM5+	-0.040445	0.025323
Q5_GM5+	-0.024737	0.017523
Q6_GM5+	0.006672	0.016751
Q7_GM5+	-0.046032	0.035031
Q8_X2+	0.001867	0.020599
Q9_X3+	0.384420	0.009371
Q10_X5+	-0.098031	0.013079
Q11_X5+	0.017007	0.057539
Q12_X5+	0.054982	0.018377



Other programs:

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ISODISPLACE: a web-based tool for exploring structural distortions

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http://stokes.byu.edu/isodisplace.html