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# Structural Pseudosymmetry and its applications

## PSEUDOSYMMETRY SEARCH:

We know a structure with space group H and we want to know if it is close to a configuration of higher symmetry

? → H

pseudosymmetry search

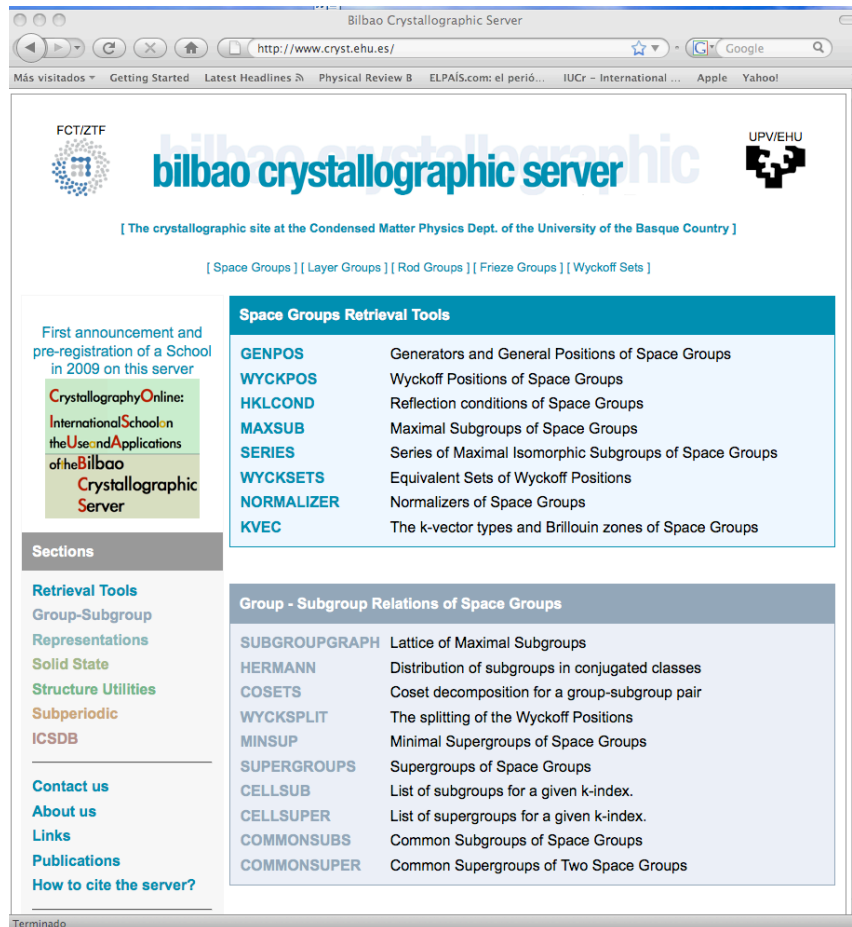
We search for a structure with space group G (supergroup of F) such that:

**Structure G = Structure F + small (symmetry-breaking) distortion**

## **Pseudosymmetry detection can be useful for :**

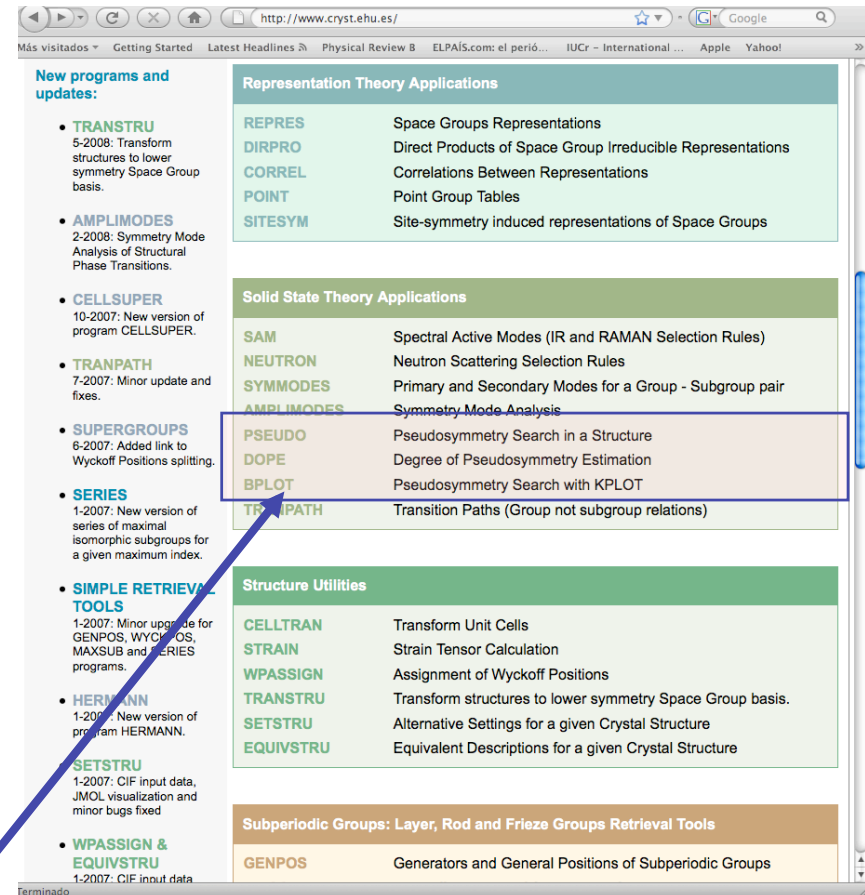
- Prediction of symmetry and structure of other phases.
- Prediction of phase transitions.
- Identification of ferroic materials: ferroelectrics, ferroelastics.
- Determination of an optimized virtual parent structure.
- Detection of false symmetry assignments (overlooked symmetry).
- Identification of the symmetry of theoretical structures calculated without symmetry restrictions (ab-initio calculations).

# Pseudosymmetry search in www.cryst.ehu.es:



The screenshot shows the homepage of the Bilbao Crystallographic Server. The header includes the logo and the text "bilbao crystallographic server" and "UPV/EHU". Below the header, there are navigation links for "Space Groups", "Layer Groups", "Rod Groups", "Frieze Groups", and "Wyckoff Sets". The main content area is divided into several sections:

- Space Groups Retrieval Tools:** A table listing tools like GENPOS, WYCKPOS, HKLCOND, MAXSUB, SERIES, WYCKSETS, NORMALIZER, and KVEC with their descriptions.
- Group - Subgroup Relations of Space Groups:** A table listing tools like SUBGROUPGRAPH, HERMANN, COSETS, WYCKSPLIT, MINSUP, SUPERGROUPS, CELLSUB, CELLSUPER, COMMONSUBS, and COMMONSUPER with their descriptions.
- Retrieval Tools:** A sidebar menu with links for Group-Subgroup, Representations, Solid State, Structure Utilities, Subperiodic, ICSD, Contact us, About us, Links, Publications, and How to cite the server?



The screenshot shows the "New programs and updates" page of the Bilbao Crystallographic Server. It features a list of updates on the left and several application categories on the right:

- New programs and updates:** A list of updates including TRANSTRU, AMPLIMODES, CELLSUPER, TRANPATH, SUPERGROUPS, SERIES, SIMPLE RETRIEVAL TOOLS, HERMANN, SETSTRU, and WPASSIGN & EQUIVSTRU.
- Representation Theory Applications:** A table listing tools like REPRES, DIRPRO, CORREL, POINT, and SITESYM with their descriptions.
- Solid State Theory Applications:** A table listing tools like SAM, NEUTRON, SYMMODES, AMPLIMODES, PSEUDO, DOPE, BPLOT, and TRANPATH with their descriptions.
- Structure Utilities:** A table listing tools like CELLTRAN, STRAIN, WPASSIGN, TRANSTRU, SETSTRU, and EQUIVSTRU with their descriptions.
- Subperiodic Groups: Layer, Rod and Frieze Groups Retrieval Tools:** A table listing the GENPOS tool.

A blue arrow points from the text "three programs for pseudosymmetry search" at the bottom to the PSEUDO, DOPE, and BPLOT entries in the Solid State Theory Applications table.

three programs for pseudosymmetry search

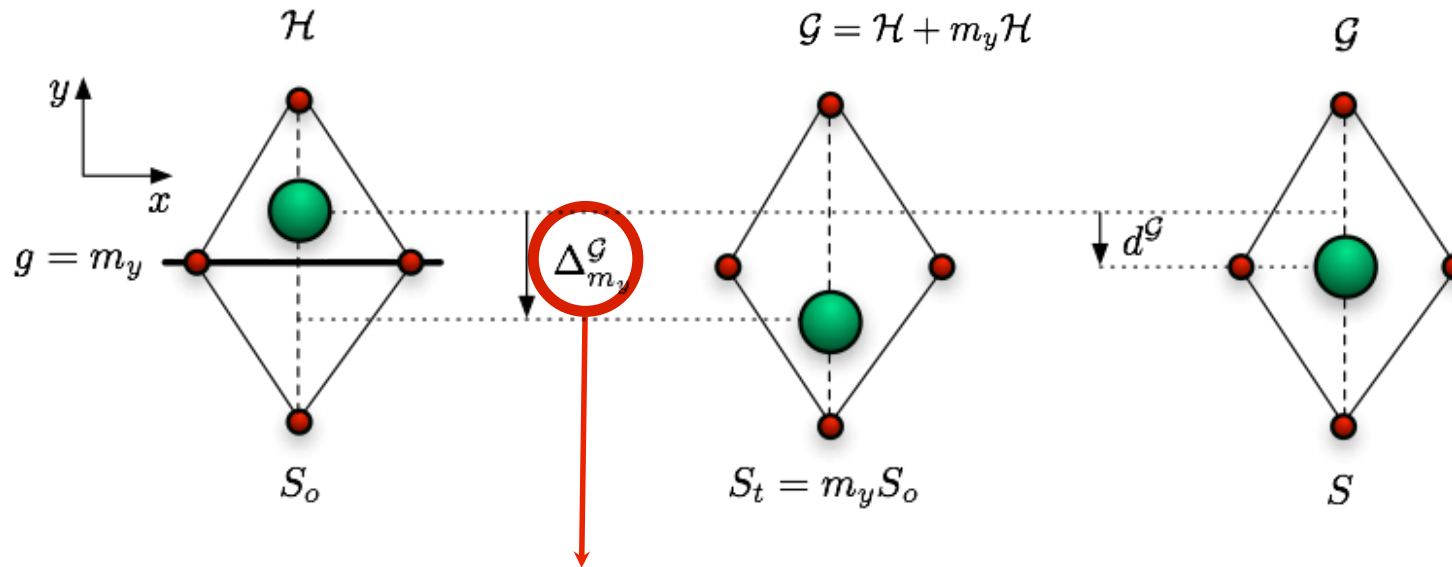
## PROGRAMS FOR PSEUDOSYMMETRY SEARCH:

**PSEUDO** - Atomic displacement method

**DOPE** - Electron density method

**BPLOT** - KPLOT method (R. Hundt)

## PSEUDO. ATOMIC DISPLACEMENTS METHOD



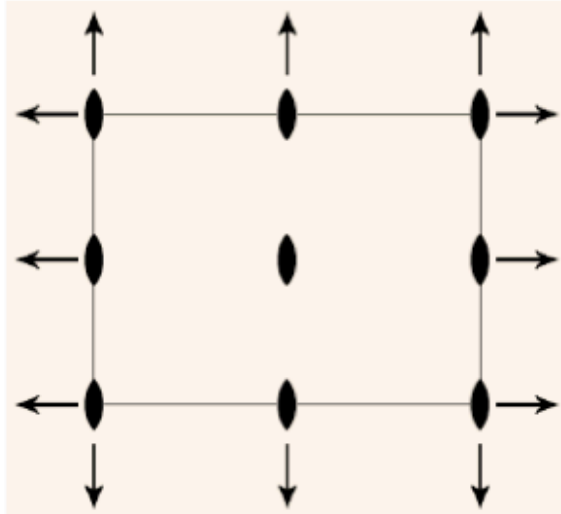
**Maximal distance between all compatible atom pairings**

**Assumption:**

The high symmetry phase is described by a supergroup of the initial space group.

$$\mathbf{G} = \mathbf{H} + g_2 \mathbf{H} + \dots + g_k \mathbf{H}$$

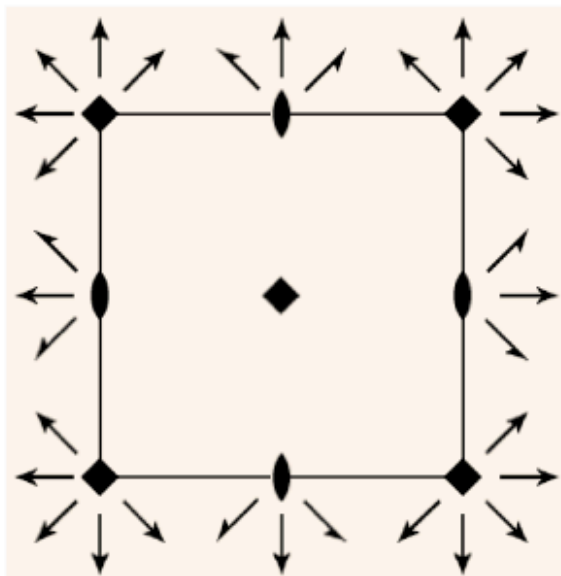
## Supergroups of the same type



$$\mathcal{H} = P222$$

$$\mathcal{G} = P422$$

$$P422 = P222 + (4|\omega)P222$$



	4 en	$\omega$	$\mathcal{G}$
$4_z$	$(0, 0, 0)$	$(0, 0, 0)$	$(P422)_1$
$4_y$	$(0, 0, 0)$	$(0, 0, 0)$	$(P422)_2$
$4_x$	$(0, 0, 0)$	$(0, 0, 0)$	$(P422)_3$
$4_z$	$(\frac{1}{2}, 0, 0)$	$(\frac{1}{2}, \frac{1}{2}, 0)$	$(P422)'_1$
$4_y$	$(\frac{1}{2}, 0, 0)$	$(\frac{1}{2}, 0, \frac{1}{2})$	$(P422)'_2$
$4_x$	$(0, \frac{1}{2}, 0)$	$(0, \frac{1}{2}, \frac{1}{2})$	$(P422)'_3$

# DOPE ELECTRON DENSITY METHOD

ELECTRON DENSITY

$$\rho(\mathbf{r}) = \rho_0^g(\mathbf{r}) + \Delta\rho(\mathbf{r})$$

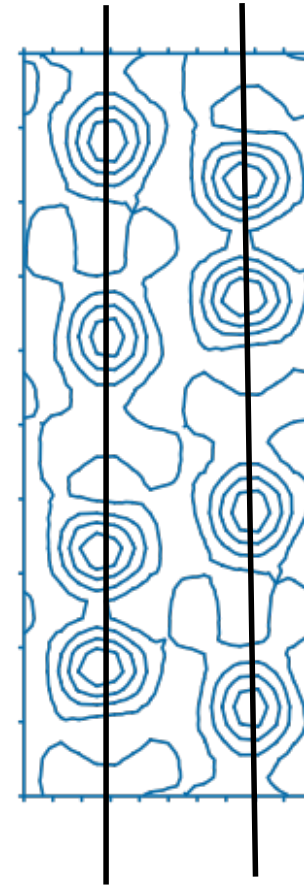
DEGREE OF DISSYMMETRY

$$\gamma = \frac{\int_V |\Delta\rho(\mathbf{r})|^2 dV}{\int_V |\rho(\mathbf{r})|^2 dV}$$

DEGREE of PSEUDOSYMMETRY

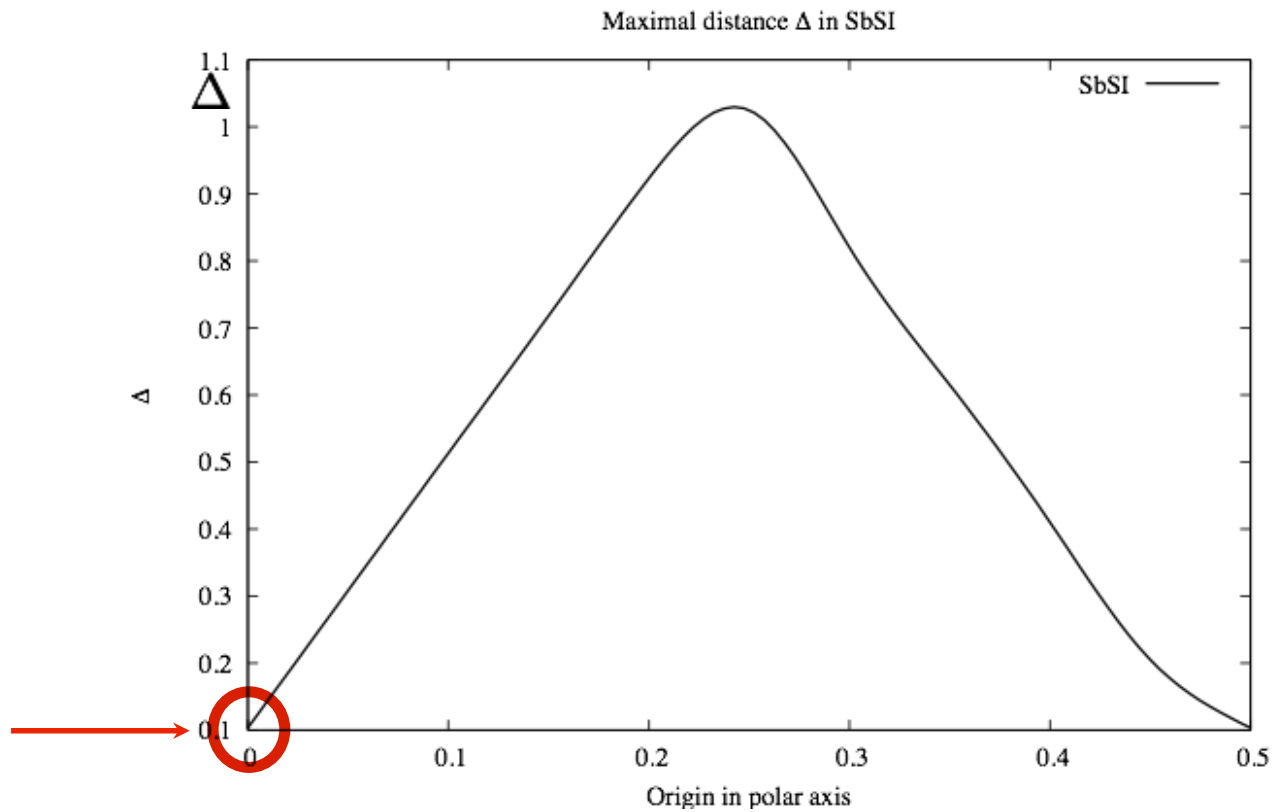
$$\eta(W_k, \omega_k) = \frac{\sum_{\mathbf{S}} F^*(\mathbf{S}) F(\mathbf{S}W_k) e^{2\pi i \mathbf{S} \omega_k}}{\sum_{\mathbf{S}} |F(\mathbf{S})|^2}$$

$$\gamma = 1 - \frac{1}{N} \sum_k \eta g_k$$





# THE FERROELECTRIC CASE: POLAR GROUPS



**The origin in the polar axis is chosen for the minimum distance....**

# Search of ferroelectrics as pseudosymmetric polar structures

two necessary conditions to be a ferroelectric:

(Kroumova et al. 2002)

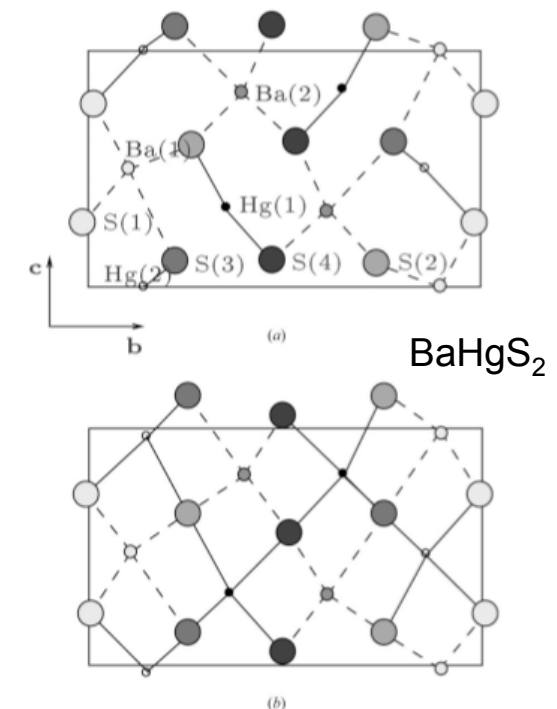
- Polar symmetry group (it should allow non-zero polarization)
- Pseudosymmetry with respect to a non-polar symmetry group – (the polar distortion should be small and “multistable”)

Pseudosymmetric structures among the compounds with symmetry  $Pmc2_1$ .

$d_{\max}^y$  is the absolute value of the maximal displacement along [010]. For a description of the remaining columns see Table 2.

Compound	$G$	$\epsilon$	$d_{\max}^y$	$d_{\max}^z$	$d_{\max}^{MC}$	$d_{\max}^{rel}$
(*) $(NH_2)_2CS$	$Pnma$	0.028	0.348	0.218	0.146	0.290
(*) $CuAgS$	$Cmcm$	0.038	0.394	0.227	0.178	0.301
(*) $CsEuNaNb_5O_{15}$	$Pmmm$	0.449	0.178	0.310	0.314	0.620
$Ca_3Mn_{1.2}Fe_{1.8}O_8^\dagger$	$Pnma$	0.478	0.223	0.343	–	0.686
$BaHgS_2$	$Pbam$	0.284	0.423	0.361	0.457	0.675
$Ca_3TiFe_2O_8^\dagger$	$Pnma$	0.460	0.347	0.421	–	0.761
$Nd_4GeO_8$	$Cmcm$	0.963	0.469	0.439	0.509	0.834
$Sr(OH)_2(H_2O)$	$Pnma$	0.119	0.388	0.447	–	0.895
$(Fe_{0.3}Mn_{0.7})Ta(O_2)O_2^\dagger$	$Pnma$	0.149	0	0.448	–	0.896
$\beta$ - $Ba(OH)_2(H_2O)$	$Pnma$	0.088	0.404	0.468	–	0.937
$NaBa_6Nd(SiO_4)_4$	$Pnma$	–0.489	0.280	0.536	0.554	1.073
$Na(AlSi_2O_6)(H_2O)_{1.1}$	$Pnma$	0.467	0.666	0.551	–	0.981
$La_2Fe_{1.76}S_5$	$Pnma$	–0.008	0.099	0.677	–	1.355
$CaPtP$	$Pmc2_1$		0.179	0.398		0.796
$KCu(CO_3)F$	$Am2$		0.467	0.501		1.002

$\dagger$  Not considered as possible ferroelectrics (see text).



**Figure 3**  
Schematic projection in the plane  $bc$  of the polar structure with symmetry  $Pmc2_1$  (a) and the calculated non-polar structure with symmetry  $Pbam$  (b) for  $BaHgS_2$ . The non-polar structure is represented with respect to the basis of the subgroup; the transformation is given in Table 3.

## Known Ferroelectrics with space group $Pna2_1$

Compound	$\mathcal{G}$	$[i]$	$\Delta_{\max}(\text{\AA})$
$\text{Nb}_6\text{I}_{11}$	<i>Pccn</i>	2	0.547
$\text{D}_{0.45}\text{Nb}_6\text{I}_{11}$	<i>Pccn</i>	2	0.745
$\text{NaTaO}_3$	<i>Pnma</i>	2	0.232
$\text{LaYbO}_3$	<i>Pnma</i>	2	0.347
$\text{RbGeBr}_3$	<i>Pnma</i>	2	0.536
$\text{K}_2\text{SeO}_4$	<i>Pnma</i>	2	0.539
$\text{Cs}_2\text{BeF}_4$	<i>Pnma</i>	2	0.174
$\text{Rb}_2\text{BeF}_4$	<i>Pnma</i>	2	0.171
$\text{K}_2\text{BeF}_4$	<i>Pnma</i>	2	0.338
$\text{Rb}_2\text{ZnBr}_4$	<i>Pnma</i>	2	0.131
$\text{Rb}_2\text{ZnCl}_4$	<i>Pnma</i>	2	0.463
$\text{K}_2\text{ZnCl}_4$	<i>Pnma</i>	2	0.177
$\text{SbSI}$	<i>Pnma</i>	2	0.103
$\text{SbSBr}$	<i>Pnma</i>	2	0.109
$\text{SbNbO}_4$	<i>Pnna</i>	2	0.421
$(\text{BiO})_4(\text{NbO}_4)\text{Cl}$	<i>Pbcn</i>	2	0.623
$\text{CsTiO}(\text{AsO}_4)$	<i>Pnna</i>	2	0.447
$\text{KTiO}(\text{AsO}_4)$	<i>Pnna</i>	2	0.610
$\text{TlTiO}(\text{PO}_4)$	<i>Pnna</i>	2	0.408

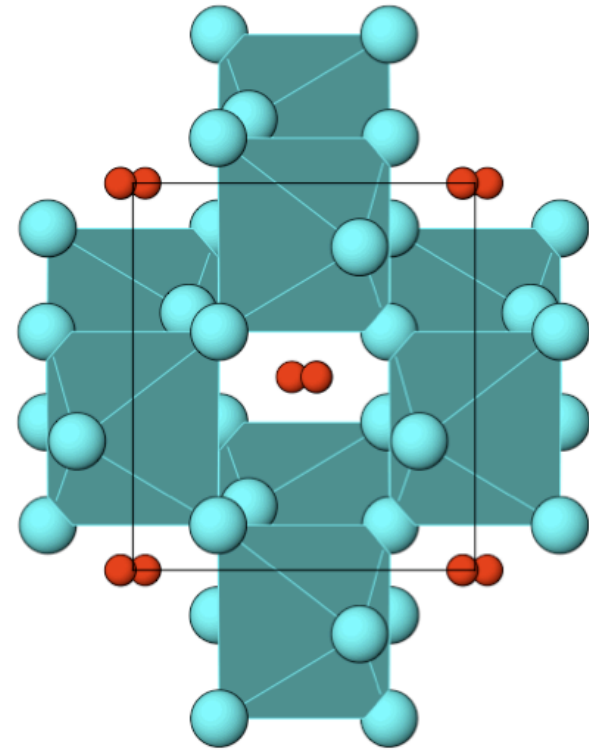
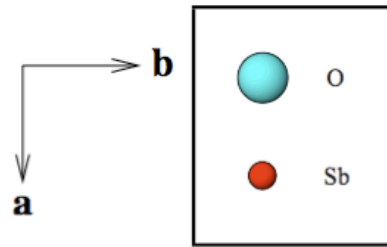
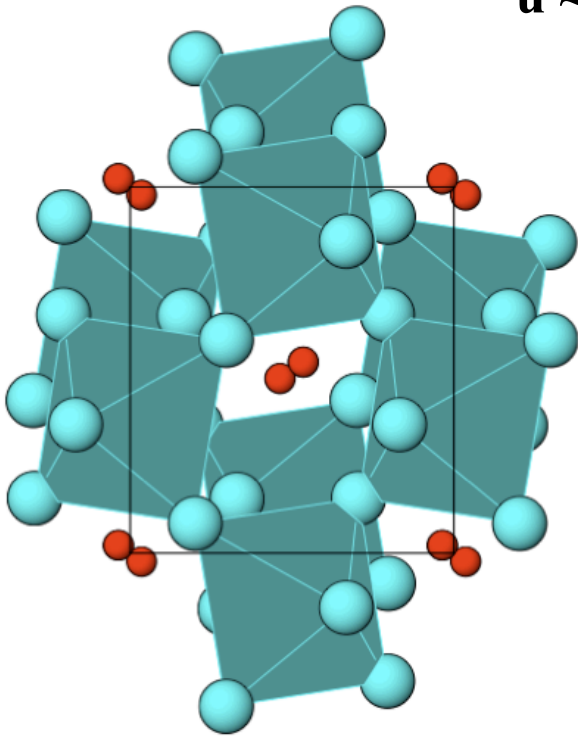
## Possible Ferroelectrics with space group $Pna2_1$

Compound	$\mathcal{G}$	$[i]$	$\Delta_{\max}(\text{\AA})$
$\text{Sb}_2\text{O}_4$	$Pnna$	2	0.581
$\text{PbNCN}$	$Pnma$	2	0.193
$\text{NaIO}_3$	$Pnma$	2	0.194
$\text{YScS}_3$	$Pnma$	2	0.179
$\text{CeSiP}_3$	$Pnma$	2	0.648
$\text{SmBeF}_4$	$Pnma$	2	0.325
$\text{K}_3\text{AsS}_4$	$Pnma$	2	0.227
$\text{WPO}_5$	$Pnma$	2	0.457
$\text{Sr}_3\text{Sb}_4\text{S}_9$	$Pnma$	2	0.230
$\text{Be}_4\text{Pr}_9\text{O}_{20}$	$Pnma$	2	0.246
$\text{Ca}_{0.84}\text{Sr}_{1.16}\text{SiO}_4$	$Pnma$	2	0.580
$\text{Tl}_{1.1}\text{AlSiO}_4$	$Pnma$	2	0.590
$\text{Na}_2\text{UO}_2\text{P}_2\text{O}_7$	$Pnma$	2	0.559
$\text{TlSnPS}_4$	$Pnma$	2	0.488

Example:  $\text{Sb}_2\text{O}_4$  ( $Pna2_1 \xrightarrow{(2)} Pnna$ )

$$\Delta = 0.581\text{\AA} \text{ y } \eta_g = 0.641\text{\AA}$$

$$u \approx 0.3 \text{\AA}$$



## Search of maximal pseudosymmetry through a chain of minimal supergroups:

(stepwise detection of pseudosymmetry for successive minimal supergroups)

If a structure of symmetry  $H$  is pseudosymmetric for a supergroup  $G$ , it will be pseudosymmetric for all intermediate subgroups  $H_i$ :  $G > \dots > H_i > \dots > H$

