Materials 218/UCSB: Phase transitions and polar materials

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Background:

- Intrinsic stability of thermodynamic systems (after H. B. Callen, Thermodynamics and an introduction to thermostatistics, 2nd Edn.):

  The entropy function S for a thermodynamic one-component system is:

  $$S = S(U, V)$$

  where U is the internal energy and V is the volume. By definition $\mathrm{d}S = 0$ and $\mathrm{d}^2S < 0$ describe equilibrium conditions. The first condition is that the entropy is at an extremum, and the second condition specifies that the extremum is a maximum.

  If N is fixed, $S = S(U, V)$ and one can show by perturbing U and V slightly (both separately and together) that for the system to be *stable*, three conditions can be obtained:

  $$\left(\frac{\partial^2 S}{\partial U^2}\right)_V \leq 0$$

  $$\left(\frac{\partial^2 S}{\partial V^2}\right)_U \leq 0$$

  $$\left(\frac{\partial^2 S}{\partial U^2}\right)\left(\frac{\partial^2 S}{\partial V^2}\right) - \left(\frac{\partial^2 S}{\partial U \partial V}\right) \geq 0$$

- Some of these conditions translate into more familiar ones. For example, suitable manipulation suggests that:

  $$\left(\frac{\partial^2 S}{\partial U^2}\right)_V = \frac{1}{T^2}\left(\frac{\partial T}{\partial U}\right)_V = -\frac{1}{T^2 C_V} \leq 0$$

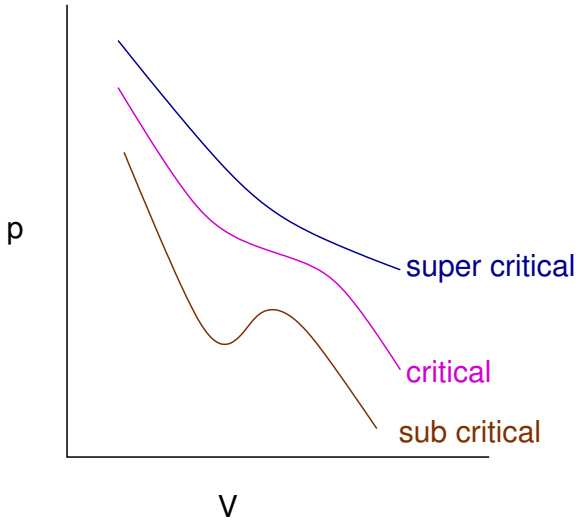
  Which tell us, since T must always be positive, that C_V must always be positive for a system to be stable. In other words, when heat is provided to a system at constant volume, its temperature *must* increase.

  Along the same lines, the isothermal compressibility

  $$\kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T > 0$$

  If at constant T, pressure is applied on a system, the volume of the system *must* decrease.

  There can exist regions in phase diagrams of 1-component system where the system might try and violate these stability conditions. Near these regions, *phase transitions* occur that prevent such violation.

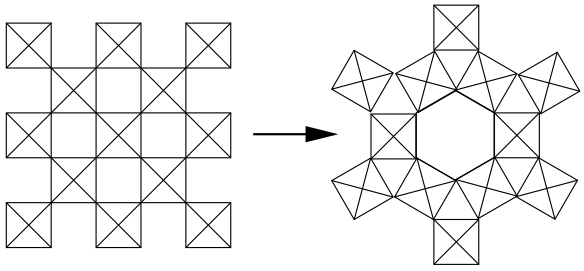


Consider isotherms of the van der Waals equation of state. In the lowest sub-critical trace shown above, there are regions which are clearly unstable as they correspond to regions with $\kappa_T < 0$. At these points, one can expect phase transitions.

- A study of phase transitions (or transformations) is particularly important in the solid state, since in many solid materials, properties (electrical, magnetic, mechanical ...) are inalienably inked with phase transitions that the material might have undergone, or might undergo.

Phase transitions and crystals (after Megaw):

- Reconstructive: There is complete fragmentation of the crystal associated with there being no orientational relationship between the parent and daughter phase:



An example is the phase transition from the perovskite lattice (left above) to the hexagonal tungsten bronze structure (right above). The A atoms in the structure are not shown.

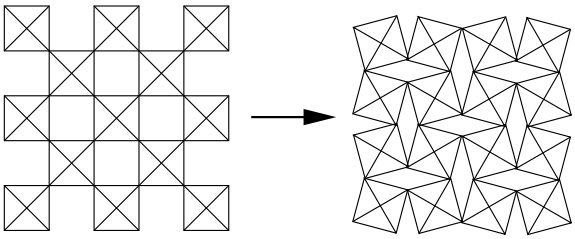
- Close orientational relationships; interchange of atoms, randomly, by diffusion: *Substitutional order-disorder:*

  This is the kind of relationship seen on going from the $Fm\bar{3}m$ alloy $Cu_{0.75}Au_{0.25}$ with the Cu structure to the perovskite-like intermetallic $Pm\bar{3}m$ Cu_3Au. In the alloy, the fcc lattice sites are randomly occupied by (on average) $Cu_{0.75}Au_{0.25}$.

- No close orientational relationships, with large changes of shape; no diffusion: *Martensitic:*

  This is the kind of phase transition that one has on going from the CsCl structure to the NaCl structure (happens to KI upon heating)

– Close orientational relationships: Pure displacive:
Obtained by mild shearing of structures. No bond-breaking or making. An example is going from a cubic perovskite to an orthorhombic perovskite:



– Close orientational relationships: Order-disorder by H hopping.

– Close orientational relationships: Orientational switching, ordering (eg C_{60}).

– Intra-atomic order disorder: Cooperative Jahn-Teller distortions, Verwey transitions.

The free energy across phase transitions and Landau theory:

Please see the handout.

$BaTiO_3$:

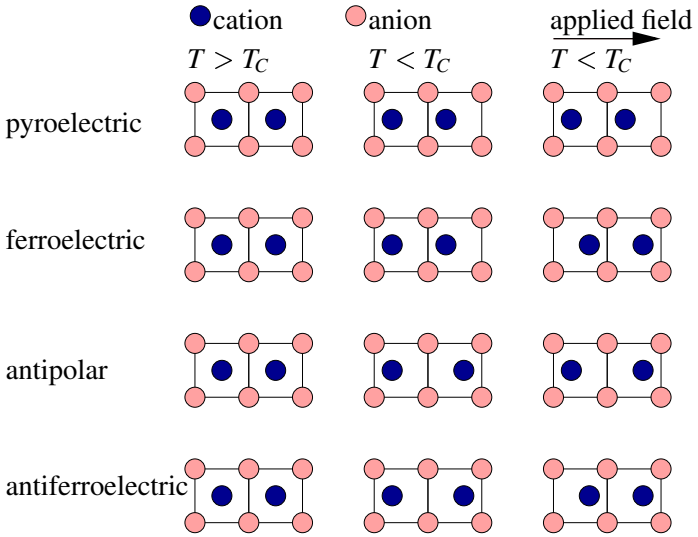
$BaTiO_3$ is one of the most widely used ferroelectric materials, and has been investigated in detail since its first preparation in the early 1940's. Above 393 K, it is cubic, and has the ideal perovskite structure. It is paraelectric, meaning that electric polarization (the number of electric dipoles per unit volume) increase linearly with the applied electric field.

The *tolerance* factor of $BaTiO_3$ defined:

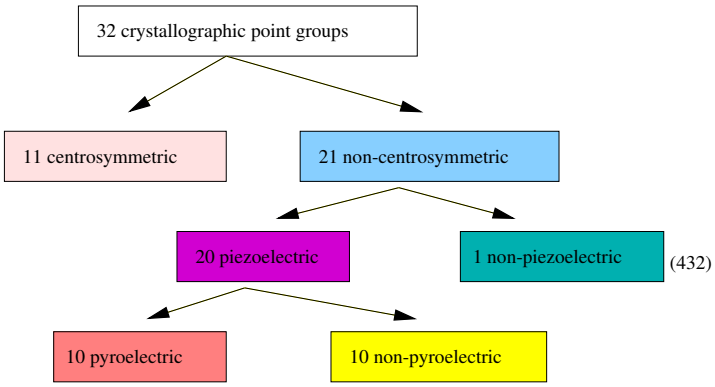
$$t = \frac{(r_{\mathrm{Ba}} + r_{\mathrm{O}})}{\sqrt{2}(r_{\mathrm{Ti}} + r_{\mathrm{O}})}$$

is greater than 1 (it is 1.07) which means that Ba^{2+} is too large to fit into the space created by eight TiO_6 octahedra at the corners of the perovskite cube. In addition, Ti^{4+} has the d^0 configuration. This is a configuration prone to go *off-center* which is good for ferroelectricity.

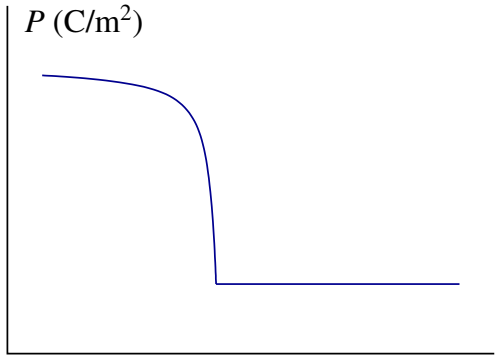
- Crystals comprising cations and anions can be classified into four types, according to their *polar* behavior:

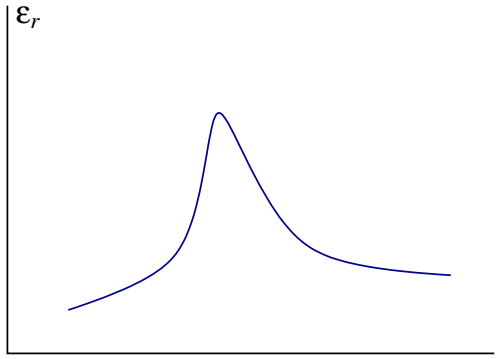


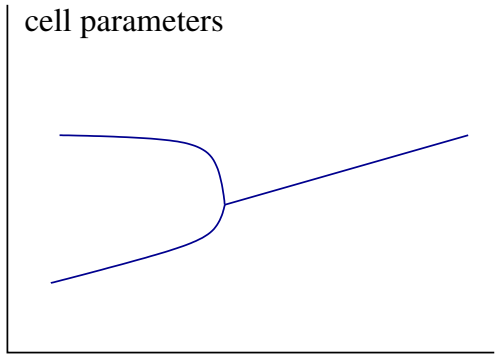
- Piezoelectric materials: There is coupling between electrical and mechanical energies. For example, an applied stress results in the generation of polarization.
- Pyroelectric materials: A material with a temperature dependent polarization. This requires a unique polar axis.
- Ferroelectrics: A subgroup of pyroelectric materials in which the spontaneous polarization can be reoriented between "equilibrium" states by applying an electric field. All ferroelectrics are both pyroelectric and piezoelectric.
- The possibility of inorganic crystals being polar (pyroelectric or piezoelectric) is strictly a function of their point group symmetry:



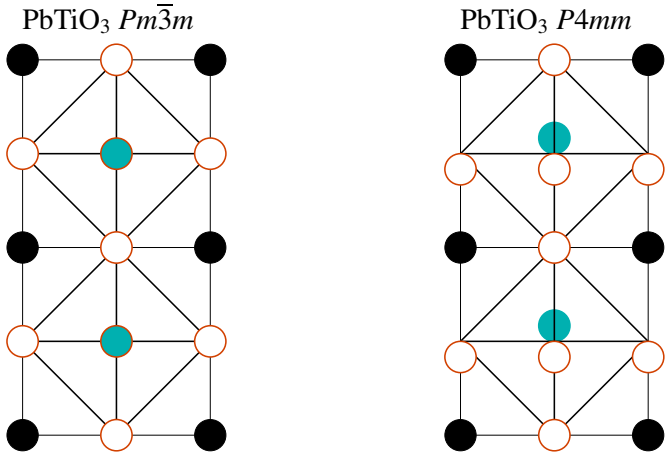
- The ferroelectric phase transition (for example, in $PbTiO_3$) is characterized by the development of a spontaneous (zero field) polarization, changes in the dielectric constant, and crystal structural changes.:



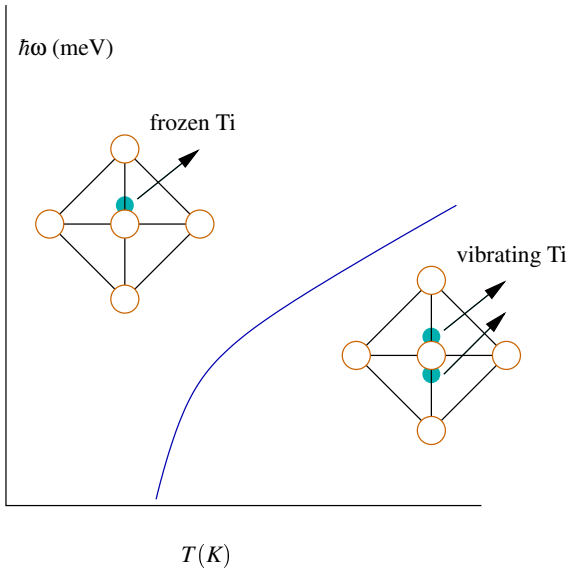




- At the origins of such a phase transition are developments of a dipole within the unit cell, due to the centers of positive and negative charges not coinciding:

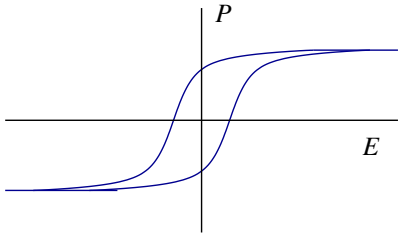


- In the particular case of $PbTiO_3$, the phase transition from the cubic, paraelectric phase to the tetragonal ferroelectric phase (a displacive phase transition) is associated with the freezing of a phonon mode that is referred to as the "soft mode". Phonon modes are specific vibrational modes of the crystal lattice. In the case of $PbTiO_3$, this phonon mode is associated with the Ti atom in the center of the octahedron:

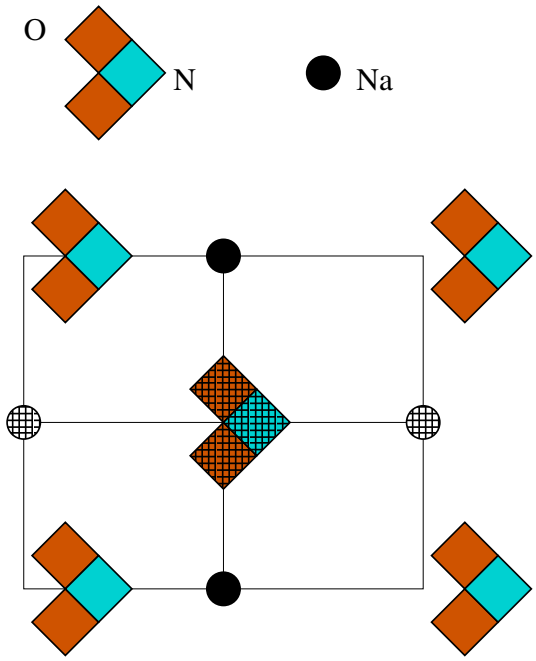


The frequency (energy) of the soft mode goes to zero as the phase transition is approached.

- Ferroelectric materials are also characterized by hysteresis of the polarization below the ferroelectric T_C, just as are ferromagnets are characterized by a hysteresis of the magnetization:



- As is true for ferromagnets, the hysteretic behavior is a consequence of the presence of domains in the material.
- Some materials undergo an *order-disorder* phase transition from the paraelectric phase to the ferroelectric phase. An example is $NaNO_2$ (sodium nitrite):

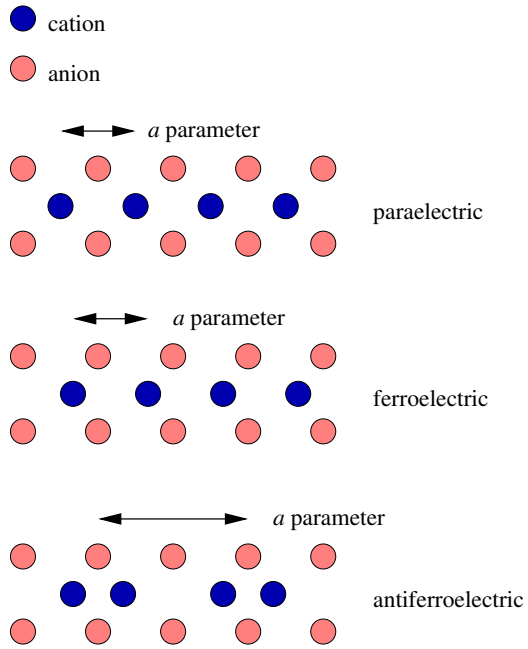


Room temperature ferroelectric structure of $NaNO_2$ projected on (001). The rigid NO_2^- groups have been shown as little chevrons, and the Na^+ ions as circles. Hatching indicates that the atoms are at a height of -1/2.

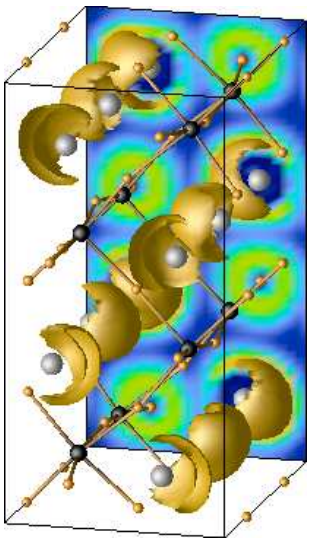
Above the phase transition at 438 K, the structure is non-polar and has the $Immm$ space group. Below this temperature, the material is ferroelectric and has the space group $Im2m$; the ferroelectric structure is displayed.

The dipole moment is lost in the high temperature structure because of disorder. Half the chevrons point to the left and half to the right, and correspondingly, the Na ions also occupy two different sites at random.

- Antiferroelectrics: These are usually characterized by antiparallel dipole moments in the unit cell. The formation of antiparallel moments (as in antiferromagnetic systems) results in the formation of larger unit cells.

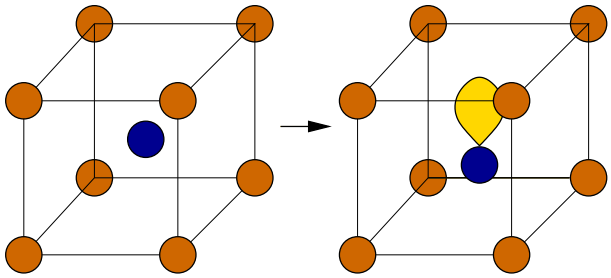


- An example of an antiferroelectric is $PbZrO_3$, which is cubic ($Pm\bar{3}m$), paraelectric above 503 K. Below this temperature, a combination of *two* effects, the tendency of the ZrO_6 octahedra to tilt as a consequence of the tolerance factor being less than 1, and the tendency of the Pb^{2+} ions to go off-center, result in the antiferroelectric, orthorhombic crystal structure.



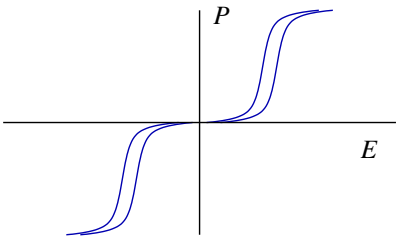
In this depiction of the crystal structure of $PbZrO_3$, the "lone pairs" on the Pb atoms are visualized using DFT calculations of the electronic structure. Note that the "lone pairs" creates a structural distortion that cancels itself.

- What are lone pairs ? The three ions Tl^{+}, Pb^{2+} and Bi^{3+} have the electronic configuration $[Xe]4f^{14}5d^{10}6s^{2}$. The pair of s electrons in the valence shell (the lone pair) should have spherical symmetry if they retain "pure" s character. However, they like to mix with anion (oxygen) p orbitals, and this mixing results in their going "off center". Such "off-centering" is a good recipe for obtaining polar behavior.



Sketch displaying the tendency of a lone pair ion (blue) such as Pb^{2+} to go off-center in its coordination polyhedron, leaving in the center of the polyhedron, the s^2 lone pair. Such a sketch is quite accurate for describing the crystal structure of PbO in the litharge modification.

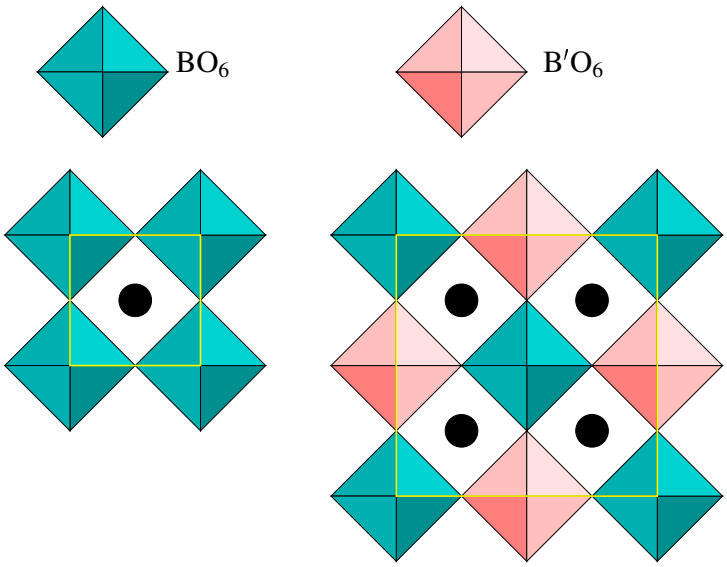
- Antiferroelectrics do not display hysteresis, except at high fields, where they develop separate loops at positive and negative fields. A similar dependence of magnetization on the magnetic fields is seen in *metamagnets*.



- Ordered double perovskites (elpasolites) and relaxor ferroelectrics:

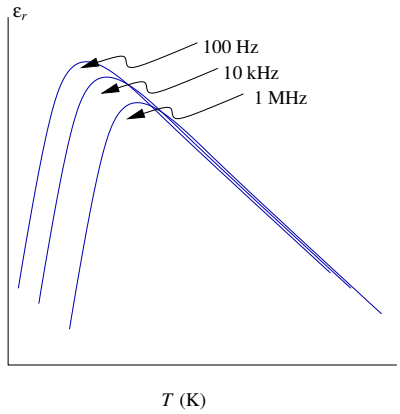
- Ordered double perovskites have the general formula $A_2BB'O_6$. One kind of octahedra in the structure is BO_6 and the other is $B'O_6$. For the octahedra to be *distinct*, meaning that there is no mixing of B and B′ in the lattice sites of the structure, there must usually be a large difference in size and charge between B and B′. For example, in the ordered double perovskite Ba_2MgWO_6, there is no mixing of Mg^{2+} and W^{6+} on a single lattice site.

  Instead of the $Pm\overline{3}m$ space group of simple ideal perovskites (which have cell parameters of the order of 4 Å), ideal double perovskites crystallize in the $Fm\overline{3}m$ space group with a cell parameter around 8 Å. Indeed, the two kinds of octahedra in the elpasolite structure are arranged as in the rock salt structure:



The yellow squares indicate the unit cell.

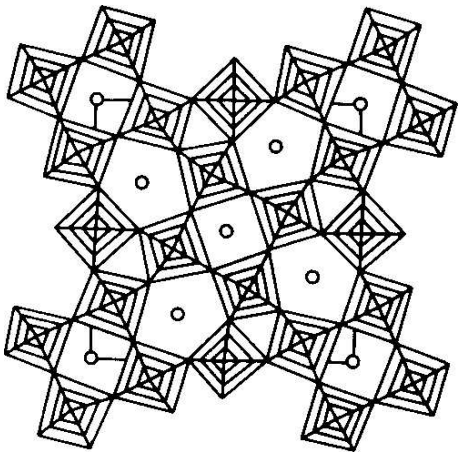
- Many elpasolite-like compositions with Pb in the A-site display disorder of some sort, because the ordering between the B and B′ sites is not complete. Many of these disordered materials display *relaxor* behavior. For example, $Pb_2Mg_{2/3}Nb_{4/3}O_6$ (PMN), Pb_2ScNbO_6 (PSN) etc. In PMN and PSN, there are two different kinds of octahedra in the structure; one that is Nb-rich and the other that is Nb-poor. Such disorder seems to be important for observing *relaxor* behavior, which is characterized by:
  - Broad phase transitions
  - Dispersion characteristics of the dielectric constant: The $\epsilon - T$ behavior is frequency dependent.



- Relaxors are useful since they have a high dielectric constance even at radio frequencies and they saturate at low voltages. Because of the broad phase transition, the T dependence of ϵ_r does not create problems in devices. In addition, the hysteresis is small, the energy densities are high and the materials are field-tunable.

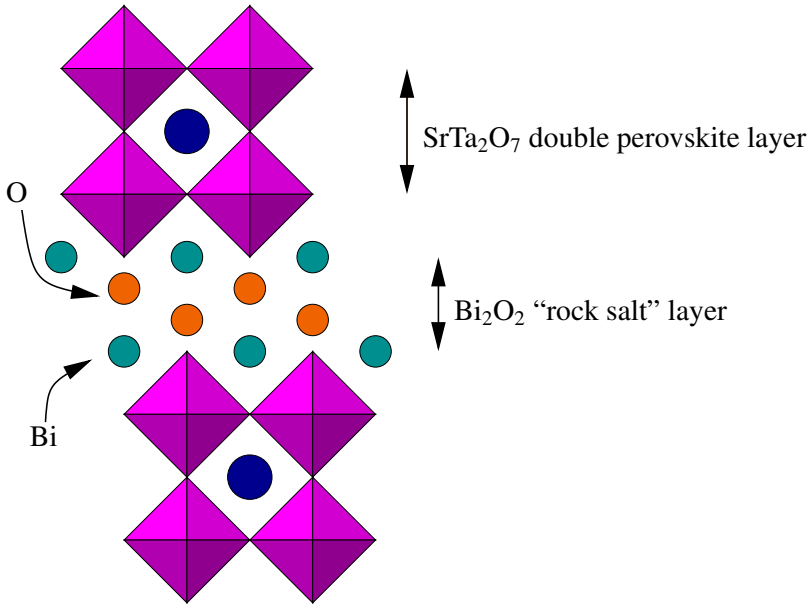
Some other structure types where polar behavior is found

- The tetragonal tungsten bronze (*eg.* $SrNb_2O_6$):



The structure can be constructed from the perovskite lattice through suitable crystallographic shear. Compare with the hexagonal tungsten bronze structure of the previous class.

- The Aurivillius phases: (*eg.* $SrBi_2Ta_2O_9$):



These are *intergrowth* phases comprising double “rock-salt” like Bi_2O_2 layers intergrown with perovskite layers. The general formula of this family of phases is $Bi_2A_{n-1}B_nO_{3n+3}$; $n = 1, 2, 3 \ldots$ The A site is like the A site in the perovskite structure, and the B site is like the B site in the perovskite structure. Typically, A = Pb, Bi, Na, K, Ca, Sr or the rare-earths, and B = Ti, Nb, Ta, Mo, W *etc.*

Examples: $n = 1$: Bi_2WO_6; $n = 2$: $Bi_2SrTa_2O_9$; $n = 3$: $Bi_4Ta_3O_{12}$