All of these materials display thermal phase transitions to a compound with a polar point group.
Thermal evolution of a ferroelectric

Ferroelectric soft mode: A vibration that goes to 0 frequency at the transition (upon cooling to the polar phase)
The original discovery by Valacek in Rochelle salt, in 1921. The Sawyer-Tower circuit for measurements is shown below.

Rochelle salt: Potassium sodium tartrate tetrahydrate, (KNaC₄H₄O₆·4H₂O)

David Brewster in 1824 demonstrated piezoelectric effects thereon, which led to him naming the effect pyroelectricity.

From H. W. Megaw, Ferroelectricity in Crystals, Methuen, London, 1957
Hydrogen-bonded ferroelectricity in Rochelle’s salt.

Fig. 2.1. Rochelle salt: projection of structure on 001. Figures beside atom give heights above plane $z = 0$ in hundredths of cell edge; to convert into Ångström units multiply by $c/100$. Positions of screw axes indicated by arrows. Environments of representative atoms shown by dotted lines; where these are crossed by a short line at right angles, they involve an atom in the cell vertically above or below that whose height is marked.

From H. W. Megaw, Ferroelectricity in Crystals, Methuen, London, 1957
Fig. 1.5. Dielectric hysteresis loops for Rochelle salt at different temperatures (Sawyer and Tower, 1930).
Hydrogen-bonded ferroelectricity in potassium dihydrogen phosphate (KDP); early neutron diffraction work.

From H. W. Megaw, Ferroelectricity in Crystals, Methuen, London, 1957
Fig. 1.6. Diagrammatic illustration of twinning in a pseudosymmetric structure.

(a) Crystal above transition point (high-symmetry form)
(b), (c) Low-symmetry form: two possible orientations
(d) Twinned crystal, with low-symmetry form in both orientations.
### Classification of substances related to perovskite

<table>
<thead>
<tr>
<th>I. Substances occurring only in ideal cubic form</th>
<th>SrTiO₃, SrZrO₃, SrHfO₃, SrSnO₃, SrFeO₃, BaZrO₃, BaHfO₃, BaSnO₃, BaCeO₃, EuTiO₃, LaMnO₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>II. Substances having at least one form with a distorted small-cell structure (C = cubic, T = tetragonal, O = orthorhombic, R = rhombohedral, ? = doubtful or not fully investigated)</td>
<td>BaTiO₃ (C, T, O, R), KNbO₃ (C, T, O, R), KTaO₃ (C, ?), RbTaO₃ (C, T), PbTiO₃ (C, T)</td>
</tr>
<tr>
<td>III. Substances having distorted multiple-cell structures</td>
<td>(a) CaTiO₃, (CaZrO₃), (CdTiO₃), (CaSnO₃)</td>
</tr>
<tr>
<td></td>
<td>(b) NaNbO₃, (NaTaO₃)</td>
</tr>
<tr>
<td></td>
<td>(c) PbZrO₃, PbHfO₃</td>
</tr>
<tr>
<td></td>
<td>(d) WO₃</td>
</tr>
<tr>
<td></td>
<td>(e) PbTiO₃ (low-temp.), WO₃ (high-temp.), NaNbO₃ (high temp.), NaNbO₃ (low-temp.), LaCrO₃</td>
</tr>
<tr>
<td>IV. Substances having structures based on close-packing</td>
<td>(a) FeTiO₃, CdTiO₃</td>
</tr>
<tr>
<td></td>
<td>(b) LiNbO₃, (LiTaO₃)</td>
</tr>
</tbody>
</table>

Substances in brackets have not been investigated in detail and classification is partly by analogy.
Antiferrodistortive transition in SrTiO$_3$ in R-point of the Brillouin zone

$A_{1g}$ Splitting of the structural soft mode (Raman active below $T_a$)
### Polar Materials and Ferroelectrics: SrTiO₃

**Ferroelectric SM**

**Structural SM (doublet)**

**Mode frequencies on STO ceramics**

(Petzelt et al., PRB 64, 184111 (2001))

<table>
<thead>
<tr>
<th>Species</th>
<th>Activity</th>
<th>Observed</th>
<th>Activity</th>
<th>Observed</th>
</tr>
</thead>
<tbody>
<tr>
<td>$3F_{1u}$</td>
<td>IR</td>
<td>93,176,548</td>
<td>$3A_{2u}$</td>
<td>IR</td>
</tr>
<tr>
<td>$1F_{2u}$</td>
<td>HR</td>
<td>266</td>
<td>$1B_{2u}$</td>
<td>-</td>
</tr>
<tr>
<td>$1R'<em>{15}(F</em>{1g})$</td>
<td>N</td>
<td>~ 40 (soft)</td>
<td>$1A_{1g}$</td>
<td>R</td>
</tr>
<tr>
<td>$2R'<em>{25}(F</em>{2g})$</td>
<td>-</td>
<td>-</td>
<td>$2B_{1g}$</td>
<td>R</td>
</tr>
<tr>
<td>$1R_{15}(F_{1u})$</td>
<td>-</td>
<td>-</td>
<td>$1A_{1u}$</td>
<td>-</td>
</tr>
<tr>
<td>$1R_{12}(E_{g})$</td>
<td>-</td>
<td>-</td>
<td>$1A_{2g}$</td>
<td>-</td>
</tr>
<tr>
<td>$1R_{1}(A_{1g})$</td>
<td>-</td>
<td>-</td>
<td>$1A_{2g}$</td>
<td>-</td>
</tr>
</tbody>
</table>

Total

<table>
<thead>
<tr>
<th>(Γ point)</th>
<th>$3F_{1u} + 1F_{2u}$</th>
</tr>
</thead>
</table>

Mode activity

| 3 IR | 8IR + 7R |
Polar Materials and Ferroelectrics: SrTiO$_3$

![Graph showing temperature dependence of dielectric constant](image)

- **100 kHz**
- **36.2 GHz**
- **270 GHz (9 cm$^{-1}$)**
- **$\varepsilon_0$ from IR fit including $X$ mode**
- **$\varepsilon_0$ from IR fit without $X$ mode**
- **Curie-Weiss**

**Temperature (K)**
Experiment:
- crystal (Hyper-Raman)
- 2 $\mu$m-grained ceramics (BWO)
- 2 $\mu$m-grained ceramics (MW)
- 100 nm-grained ceramics (diel. meas. 100 kHz)

Theoretical model:
- 2 $\mu$m-grained ceramics, $\varepsilon(\text{GB})=100$, $\xi=7$ nm
- 100 nm-grained, $\varepsilon(\text{GB})=100$, $\xi=7$ nm
Order-disorder model for BaTiO$_3$ phase transitions

Ordered Ba

Dynamically disordered Ti
TO1 mode in BaTiO$_3$ single crystal

- Luspin_80 (IR refl.)
- Vogt_82 (HR)
- Laabidi_90 (R)
- Perry_65 (R)
- Burns_78 (R)
- Dougherty_94 (femt. ISRS)

Temperature (K): B$_1$ ? B$_2$ E A B C

Frequency (cm$^{-1}$): 0 20 40 60 80 100 120 140 160 180 200 220 240 260 280
Polar Materials and Ferroelectrics: Bulk and nanoscale BaTiO$_3$

Polar Materials and Ferroelectrics

Antiferroelectrics: The example of PbZrO$_3$