Negative Thermal Expansion Materials
Positive Thermal Expansion

Anharmonic pair potentials between atoms in the solid

- When the atoms vibrate along a line connecting the pair, the asymmetry in the potential causes an increase in the mean distance between the atoms as the temperature increases.
- Considers only the component of vibrational motion directed along the line joining the atoms.
- Atomic vibrations give rise to thermal expansion only because of anharmonicity.
Negative Thermal Expansion (NTE) Materials

A vast majority of materials expand on heating – they have a positive coefficient of thermal expansion

Some exceptions:

• Water – Ice (increase in density of liquid water between 0 and 4ºC)
• Si, Ge and some other tetrahedrally bonded crystals at low temperatures
• β - quartz at high temperatures, some ceramics and zeolites
• Materials with low or close to zero thermal expansion coefficient have many practical applications (including composites with + and – thermal expansion)
  - Invar (36% Ni-Fe alloy, magnetic, Physics Nobel prize C. Guillaume)
  - Pyrex (borosilicate glass)
  - Cordierite (Mg₂Al₂Si₅O₁₈) glass-ceramic
  - NZP (NaZr₂(PO₄)₃ ) family, also has very low thermal conductivity
  - thermostats, casserole dishes, stove-tops, CRTs, telescope mirrors, etc.
### Thermal Expansion Coefficient of Some Materials

\[ \alpha_l = \frac{(l_T - l_0)}{l_0(T - T_0)} \]

\[ \alpha_v = \frac{(V_T - V_0)}{V_0(T - T_0)} \]

<table>
<thead>
<tr>
<th>Material</th>
<th>( \alpha_l (\times 10^{-6})/K^{-1} )</th>
<th>( T/K )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si</td>
<td>+2.45</td>
<td>373–223</td>
</tr>
<tr>
<td>Cu</td>
<td>+16.64</td>
<td>293</td>
</tr>
<tr>
<td>Ice</td>
<td>-5</td>
<td>45</td>
</tr>
<tr>
<td>Ice</td>
<td>0</td>
<td>63</td>
</tr>
<tr>
<td>Ice</td>
<td>+55</td>
<td>250</td>
</tr>
<tr>
<td>NaCl</td>
<td>+39.6</td>
<td>293</td>
</tr>
<tr>
<td>Almint 99.7% Al(_2)O(_3)</td>
<td>+7.8</td>
<td></td>
</tr>
<tr>
<td>( \alpha )-Quartz</td>
<td>42</td>
<td>223–373</td>
</tr>
<tr>
<td>( \beta )-Quartz</td>
<td>0</td>
<td>575–1000</td>
</tr>
<tr>
<td>Fused Quartz</td>
<td>0.5</td>
<td>300</td>
</tr>
<tr>
<td>Invar</td>
<td>0.07</td>
<td>278–303</td>
</tr>
<tr>
<td>NaTi(_2)(PO(_4))(_3)</td>
<td>+4.2</td>
<td>300–1000</td>
</tr>
<tr>
<td>NbZr(PO(_4))(_3)</td>
<td>-2.3</td>
<td>300–1000</td>
</tr>
<tr>
<td>ZrW(_2)O(_8)</td>
<td>-9.1</td>
<td>0–300</td>
</tr>
<tr>
<td>ZrV(_2)O(_7)</td>
<td>-7.1</td>
<td>400–500</td>
</tr>
<tr>
<td>Sc(_2)(WO(_4))(_3)</td>
<td>-2.2</td>
<td>10–450</td>
</tr>
</tbody>
</table>

Zirconium tungstate (ZrW$_2$O$_8$)

- ZrW$_2$O$_8$ exhibits a negative thermal expansion over a wide temperature range, 0.3 - 1050 K
- Consists of a framework of ZrO$_6$ octahedra and WO$_4$ tetrahedra linked at corners, but with one of the corners of the WO$_4$ tetrahedra remaining unlinked
- Because the crystal structure is cubic, the negative thermal expansion is isotropic
- Thermodynamically stable only in a narrow temperature range around 1440 K, but kinetically stabilized at lower temperature by rapid quenching after synthesis.

Linear versus Transverse Motion

- ZrW\textsubscript{2}O\textsubscript{8} has rigid ZrO\textsubscript{6} octahedra linked together to rigid WO\textsubscript{6} tetrahedra
  - almost no change in the Zr-O or W-O bond length upon heating
- Oxygen atoms linking the polyhedra, however, are permitted a wide range of M-O-M angles
- Transverse vibrations of O therefore results in negative thermal expansion
  - requires high oxygen mobility in lattice
Rigid Unit Modes (RUMs)

- RUMs are modes of vibration in which the tetrahedra or octahedra move without having to distort.
- Since the energies involved in such a motion are not large, the RUMs will have low frequencies.
  - remain populated even at low temperatures.
- In the framework of rigid (or nearly rigid) polyhedra, a rotation of one unit will cause a small volume reduction.
- When all the units can rotate due to thermal motion, the units will be collectively pull the structure inwards proportional the mean-square rotation.

\[
A(\theta) = A_0 \cos^2 \theta \sim A_0 (1 - \eta_A \theta^2)
\]

\[\eta_A = \text{geometric constant specific to a given rotation mode}\]

http://www.dur.ac.uk/john.evans/webpages/perov.htm
Zirconium tungstate (ZrW$_2$O$_8$) RUMs

http://www.dur.ac.uk/john.evans/webpages/zrw2o8side_mov.html
http://www.dur.ac.uk/john.evans/webpages/zrw2o83fold_mov.html