Zeolites and Negative Thermal Expansion

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Outline

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- Overview of Zeolites
- Data Collection
- Results and Analysis
- Comparison to other Research
- Zeolites Summary
Motivation

- To better understand the reason for a negative coefficient of thermal expansion in certain zeolite structures.
- Negative Thermal Expansion: structure contracts upon heating.
Brief Overview of Project

- Zeolites are made up of one silicon and two oxygen atoms.
- Frameworks may contain linked cages, cavities or channels. These gaps in the structure are used as filters for separating molecules of different sizes, shapes, and polarity. This process is called molecular sieving.
- Some zeolite applications include things like generating medical grade oxygen, water purification, and laundry detergent.
More Overview

- Interested in four different zeolite structures. Sodalite (SOD), Zeolite-A (LTA), Faujasite (FAU), RHO.
- Used pure zeolite structures for data collection and analysis.
- Sodalite has a positive coefficient of thermal expansion, and the other three zeolite structures all show negative thermal expansion. The reason behind this behavior is not properly understood.

<table>
<thead>
<tr>
<th>Structure</th>
<th>Coefficient of Thermal Expansion (1/K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sodalite (SOD)</td>
<td>2.26E-05</td>
</tr>
<tr>
<td>Zeolite-A (LTA)</td>
<td>-4.98E-06</td>
</tr>
<tr>
<td>Faujasite (FAU)</td>
<td>-3.24E-06</td>
</tr>
<tr>
<td>RHO</td>
<td>-3.98E-06</td>
</tr>
</tbody>
</table>
Zeolite Structure Properties

- Distinct Oxygen Positions
  - SOD – One
  - LTA – Three
  - FAU – Four
  - RHO – Two

- Secondary Building Units (SBU’s)

- Cage and Bridge
Data Collection

- Si-O Bond distance (for each distinct oxygen position)
- O-Si-O Bond angles
- Si-O-Si Bond angles
- Si-Si Bond distance
Si-O Bondlengths

- Si-O Bond distance shows a trend of increasing with temperature in all of the oxygen positions.
- The rate of change of the bond distance increases as the initial bond distance is increased.
Silicon Angles

<table>
<thead>
<tr>
<th>Angle (in degrees)</th>
<th>Temperature (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>115</td>
<td>150</td>
</tr>
<tr>
<td>114</td>
<td>150</td>
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<tr>
<td>113</td>
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<td>107</td>
<td>150</td>
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<tr>
<td>106</td>
<td>150</td>
</tr>
</tbody>
</table>

- The silicon angles show almost no change in all four of the zeolites that are of interest.
- Implies that the O-Si-O angles has negligible impact on negative thermal expansion.
The oxygen angles in all the structures, except SOD, exhibit a trend of getting smaller as the temperature increases.

The slope of the oxygen angles show that the bigger the initial oxygen angle, the bigger the rate of change according to temperature.

The Si-O2-Si angle in LTA shows the greatest change in oxygen angles and LTA also has the highest negative coefficient of thermal expansion.
Si-Si Bond Distance

- Shows a negative trend in the zeolites with NTE.
- Is probably the best way to measure the NTE in these zeolite structures.
- Shows the combined effect of the oxygen angles and the Si-O bond distance.
- The Bridge oxygen atoms in the structures are the ones with the most negative slope.
Static versus Dynamic

- Static: Uses an average position of atoms to generate data. Is what is measured experimentally.
- Dynamic: Uses MD to simulate the actual position of the atoms at every time step. All the data shown before has been dynamic data.
- The static trends for the Si-O bond length and the oxygen angles show the opposite trends when compared to their dynamic counterparts.
- Could be the reason for some disagreements within other studies.
Comparisons to other results

- Villaescusa et al (2001) Studied negative thermal expansion in pure silica zeolite. Came up with two main reasons for the NTE: Rigid Unit Modes (RUM’s) and transverse vibrations of two-coordinated oxygen atoms.
  - Similarities: Si-O Bond distance increases with temperature and O-Si-O angles show no significant trend. The Si-Si bond distance decreases.
  - Differences: The Si-O-Si angles don't decrease significantly with temperature. The structure they studied (zeolite IFR) has multiple distinct silicon atoms.
Woodcock et al (1999) discusses the properties of zeolite faujasite and A1PO-17. Suggests that changes in Si-O-Si angles are the driving force for NTE. They also tried to relate the unit cell volume and thermal expansion, which turned out to be inconclusive.

- **Similarities**: The Si-Si bond distance generally decreased with increasing temperature.
- **Differences**: O-Si-O angles show a great change. I found the opposite to be true.
Summary of Zeolites

- The Si-O-Si angles decrease in LTA, FAU, and RHO. It increases in SOD.
- The Si-Si bond distance decreases when NTE is true.
- The bond distances and silicon bond angles don’t seem to have direct affect on the thermal expansion. The bond distance does have an indirect effect on the Si-Si bond distance.
- It appears that the NTE trend in zeolites is due to the oxygen angles and that effect can be seen in the Si-Si bond distances.