Ceramic Materials

Chapter 3: Bond Energy and Properties

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Goal of this Chapter is ...

to develop *semiquantitative* relationships between

- the properties of a ceramic material and
- the depth and shape of the energy well
The Bond Energy and the Physical Properties

- Bond forces / energy between ions or atoms composing a solid determine a lot of its physical properties
- Hence we can use the bond energy as a means to predict physical properties
- Examples: melting temperature, modulus of elasticity, strength, hardness

- This prediction works in a lot of cases but not in all.
- Refinement is required for crystallized solids, i.e. effect of Madelung, and for solids made up of mixed ionic-convalent bondings.
Contents

• potential well & bond energy for ionic bonding, the equilibrium distance
• bond force as a function of the inter-ionic distance, max. force, inflexion point.
• melting temperature and hardness for ionic bonded compounds
• limitation of the prediction by potential well (example of MgO / Al2O3) -> introduction of covalency (of an ionic bond)
• thermal expansion explained with the potential well
• elastic modulus
• theoretic strength of compounds
The Bond Energy for Ionic Type of Bonding

\[ E_{\text{net}} = E_{\text{att}} + E_{\text{rep}} \]

\[ E_{\text{att}} (r) = \frac{z_1 \cdot z_2 \cdot e^2}{4\pi\varepsilon_0 \cdot r} \]

\[ E_{\text{rep}} (r) = \frac{B}{r^n} \]

\[ E_{\text{net}} (r) = \frac{z_1 \cdot z_2 \cdot e^2}{4\pi\varepsilon_0 \cdot r} + \frac{B}{r^n} \]

\[ E_{\text{bond}} = \frac{z_1 \cdot z_2 \cdot e^2}{4\pi\varepsilon_0 \cdot r_0} \left(1 - \frac{1}{n}\right) \]

\( r_0 = \text{equilibrium distance} \)
Potential and Force as Function of Inter-Ionic Distance

\[ E_{\text{net}}(r) = \frac{z_1 \cdot z_2 \cdot e^2}{4\pi\varepsilon_0 \cdot r} + \frac{B}{r^n} \]

\[ F_{\text{net}}(r) = \frac{dE_{\text{net}}(r)}{dr} \]
Comparison of Potential – Inter-Ionic Distance Curves for NaCl, MgO, LiF

- MgO potential well is much deeper than for LiF and NaCl (ca 4x deeper)
- LiF potential well is a bit deeper than for NaCl.
- Same crystal structure (Rocksalt)
- Inter-Ionic Equilibrium Distances
  - NaCl $r_0=283$ pm
  - LiF $r_0=209$ pm
  - MgO $r_0=212$ pm
- Valencies are different
The Melting Temperature

The Bond strength $E_{\text{bond}}$

depends strongly on the valency and the ionic radii/distance (lattice distance).

- The bond strength $E_{\text{bond}}$ of ionic bonded compounds is directly proportional to the multiplication of its ionic charges $z_1$ and $z_2$ and inverse proportional to the equilibrium ionic distance $r_0$.
- The higher the valency the stronger the bond strength.
- The compounds MgO, NaCl and LiF crystallize in the same lattice (fcc lattice), and ionic character of the bond is prevailing (>60%).

<table>
<thead>
<tr>
<th></th>
<th>MgO</th>
<th>NaCl</th>
<th>LiF</th>
<th>Crystal Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>2852°C</td>
<td>801°C</td>
<td>848°C</td>
<td>Rocksalt</td>
</tr>
</tbody>
</table>
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**Melting Temperature of some Compounds**

<table>
<thead>
<tr>
<th>Compound</th>
<th>Ionic Distance [Å]</th>
<th>Melting Temperature [°C]</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaF</td>
<td>2.31</td>
<td>988</td>
</tr>
<tr>
<td>NaCl</td>
<td>2.81</td>
<td>801</td>
</tr>
<tr>
<td>NaBr</td>
<td>2.98</td>
<td>755</td>
</tr>
<tr>
<td>NaI</td>
<td>3.23</td>
<td>651</td>
</tr>
<tr>
<td>MgO</td>
<td>2.1</td>
<td>2800</td>
</tr>
<tr>
<td>CaO</td>
<td>2.4</td>
<td>2580</td>
</tr>
<tr>
<td>SrO</td>
<td>2.57 (Comparable)</td>
<td>2430 (decrease)</td>
</tr>
<tr>
<td>BaO</td>
<td>2.76</td>
<td>1923 (!!!)</td>
</tr>
<tr>
<td>LiF</td>
<td>2.01</td>
<td>824</td>
</tr>
<tr>
<td>NaF</td>
<td>2.311</td>
<td>988</td>
</tr>
<tr>
<td>KF</td>
<td>2.67</td>
<td>846</td>
</tr>
<tr>
<td>RbF</td>
<td>2.82</td>
<td>775</td>
</tr>
</tbody>
</table>

The melting temperature increases as the ionic distance decreases within the lattice. The melting temperature increases for increasing valency given about same ionic distance.
Hardness

as function of the inter-ionic distance and the ionic charge

<table>
<thead>
<tr>
<th>Compound</th>
<th>Ionic Distance [Å]</th>
<th>Hardness [Mohs]</th>
</tr>
</thead>
<tbody>
<tr>
<td>BeO</td>
<td>1.65</td>
<td>9</td>
</tr>
<tr>
<td>MgO</td>
<td>2.3</td>
<td>6.5</td>
</tr>
<tr>
<td>CaO</td>
<td>2.4</td>
<td>4.5</td>
</tr>
<tr>
<td>SrO</td>
<td>2.57</td>
<td>3.5</td>
</tr>
<tr>
<td>BaO</td>
<td>2.76</td>
<td>3.3</td>
</tr>
<tr>
<td>Na$^+$F$^-$</td>
<td>2.01</td>
<td>3.2</td>
</tr>
<tr>
<td>Mg$^{2+}$O$^{2-}$</td>
<td>2.3</td>
<td>6.5</td>
</tr>
<tr>
<td>Sc$^{3+}$N$^{3-}$</td>
<td>2.67</td>
<td>7-8</td>
</tr>
<tr>
<td>Ti$^{4+}$C$^{4-}$</td>
<td>2.82</td>
<td>8-9</td>
</tr>
</tbody>
</table>

The hardness increases with decreasing ionic distance, assuming constant ionic charges. The hardness increases for increasing valency, despite increasing ionic distance.
The Melting Temperature of Al\textsubscript{2}O\textsubscript{3} and MgO

\begin{align*}
\text{Al}_2\text{O}_3: & \quad 2054 \degree \text{C} \\
\text{MgO}: & \quad 2852 \degree \text{C}
\end{align*}

\text{Presumption: MgO has the lower melting temperature.}

Why?

\textbf{Criteria of Analysis:}

\begin{itemize}
  \item Ionic Distance
  \item Valency
  \item Bond Energy
  \item Lattice Energy
\end{itemize}
The Melting Temperature of Al₂O₃ and MgO

Al₂O₃: 2054 °C
MgO: 2852 °C

Presumption: MgO has the lower melting temperature. Why?

Criteria of Analysis:

- Ionic Distance
  
  \[ r_0^{Al_2O_3} = 193.5 \text{ pm}, \quad r_0^{MgO} = 212 \text{ pm} \]

- Valency
  
  \[ (z_1 \times z_2)^{Al_2O_3} = -6, \quad (z_1 \times z_2)^{MgO} = -4 \]

- Bond Energy
  
  \[ \frac{E^{Al_2O_3}_{bond}}{E^{MgO}_{bond}} = 1.64 \]

- Lattice Energy
  
  \[ \frac{E^{Al_2O_3}_{Lattice}}{E^{MgO}_{Lattice}} = 23.54 \]

The analysis based on the potential well of an ionic bonded solid is often good and correct, however not all the time!!!
The Melting Temperature of $\text{Al}_2\text{O}_3$ and $\text{MgO}$

$\text{Al}_2\text{O}_3$: 2054 °C
$\text{MgO}$: 2852 °C

We need other and better criteria !!!

Further Criterium of Analysis:

$\rightarrow$ Type of Bond: amount of covalency in the bonds for $\text{Al}_2\text{O}_3$ is higher than for $\text{MgO}$.

A measure for covalency is, for example, the difference in electronegativity of the ions. $\Delta \text{EN}^{\text{Al}_2\text{O}_3} = 1.83$, $\Delta \text{EN}^{\text{MgO}} = 2.13$
The Covalent Character of a Bond

- The covalent character of a bond increases from the left to right.
- The network structure of the bonds changes: from a 3D structure of TiO$_2$ (Rutile), to a layered structure of CdI$_2$, to a molecule lattice of CO$_2$. The melting temperature decrease in this direction, too.

TiO$_2$ idealized Rutile  
$T_m = 1857°C$

CdI$_2$ layer structure  
$T_m = 387°C$

CO$_2$ molecule lattice  
$T_m = -57°C$

MX$_2$ stoichiom., $\Delta$EN = 1.9
MX$_2$ stoichiom., $\Delta$EN = 0.97
MX$_2$ stoichiom., $\Delta$EN = 0.89

$T_m =$ melting temp.
What issues influence the amount of covalency in an ionic bond?

- Polarizing power of the cation
- Polarizibility of the anion
- Electron configuration of the cation

**MgO vs Al₂O₃**

\[ \phi^{\text{Al}^{3+}} = 60 \, \text{Å nm}^{-1}; \phi^{\text{Mg}^{2+}} = 31 \, \text{Å nm}^{-1} \]

- \( \alpha_{\text{O}^-} \) equal for both cases
- no d-electrons in both cases

![Diagram](image)

(a) ideal pair of ions (no polarization)

(b) polarized pair of ions

(c) high amount of polarizing sufficient to form a covalent bond
The Thermal Expansion Coefficient

\[ \alpha = \frac{1}{l_0} \left( \frac{\partial l}{\partial T} \right)_p \]

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Potential Energy

\[ r_{\text{min}} \quad r_0 \quad r_{\text{max}} \]

ionic distance \( r \)

maximum potential energy

energy level of the thermal vibration

\[ \star = \text{mean ion density (location) for increasing temperature} \]
Thermal Expansion of Chosen Ceramic Materials

- Metals possess a higher thermal expansion than ceramic materials
- $\alpha$ is a function of the temperature
- The higher $T$ the higher $\alpha$
- Loosely packed, non-dense structures (higher amount of bond covalency) may have very small $\alpha \rightarrow$ changement of angle of the bonds
Thermal Expansion Coefficient in case of phase transformation

- $\alpha$ is a function of temp.
- Quartz shows one transformation temperature.
  - Q. is a single crystal - the other materials are polycrystals.
- $\alpha$ of $\beta$-quartz has a negative slope, i.e. increasing temp. leads to smaller $\alpha$ (see also ZrO2)
- Quartz has a lower $\alpha$ than cristobalite because quartz bonding can change angles, and cristobalite bond angles are already more straight
- SiO2 vit. : bond angles change in all spatial directions.
Anisotropic thermal Expansion Coefficients

$\beta$-Eucryptite ($\text{LiAlSiO}_4$) = Glass Ceramic
Glass ceramics: Zerodur

Astro Space: Mirrors of future x-ray satellites

Micro lithography: Zerodur® components are used as movable elements in wafer-stepper and wafer-scanners.

Metrology: Because of its very low thermal expansion and its long-term stability, components made of Zerodur® will show excellent precision in measurements instruments and metrology.

Mechanic: Excellent machinability of Zerodur® in combination with the modern high-tech manufacturing technologies enables complex shapes.

Further Applications: Zerodur® has good transmission properties in visible and infrared spectrum and a very good optical homogeneity. Because of these properties Zerodur® is often used in optical systems.

http://www.schott.com/optics_devices/german/products/zerodur/?c=ml
Thermal Expansion and Melting Temperature of chosen chemical Elements
Thermal Expansion and Melting Temperature of chosen chemical Elements
Thermal Expansion and Melting Temperature of chosen chemical Elements

- The higher the melting temperature the deeper the potential well.

- The deeper the potential well the more symmetric it appears.

- The more symmetric the less thermal expansion
The Elastic Modulus of Materials

\[ E_{net} = \frac{z_1 \cdot z_2 \cdot e^2}{4\pi\varepsilon_0 \cdot r} + \frac{B}{r^n} \]

\[ F_{net} = \frac{dE_{net}}{dr} = \frac{z_1 \cdot z_2 \cdot e^2}{4\pi\varepsilon_0 \cdot r^2} - \frac{n \cdot B}{r^{n+1}} \]
The force – inter-ionic distance curve.

In the equilibrium point $r_0$ a tangential line exists which in a first approximation describes good the linear elastic behaviour of a solid under tensile force.
**The Elastic Modulus of Materials**

\[
\sigma = E \cdot \varepsilon \\
F = S_0 \cdot (r - r_0)
\]

\[
S_0 = \left( \frac{\partial F}{\partial r} \right)_{r=r_0}
\]

\[
E \approx \frac{S_0}{r_0}
\]

\[
E = \frac{1}{r_0} \left( \frac{\partial F}{\partial r} \right)_{r=r_0} = \frac{1}{r_0} \left( \frac{\partial^2 E_{net}}{\partial r^2} \right)_{r=r_0}
\]

**This result is important:**

1. the stiffness (elastic modulus) of a solid is directly related to the curvature of its potential – ionic distance curve. The curvature is inverse of the curvature radius.
2. compounds with stronger bonds have a higher elastic modulus (stiffness) than weak bonded compounds, and
3. compounds with a high melting temperature, i.e. ceramic materials, (deep potential well) are very stiff solids.
The Elastic Modulus

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# The Elastic Modulus

<table>
<thead>
<tr>
<th>Material</th>
<th>Young's modulus GPa</th>
<th>Density g/cc</th>
</tr>
</thead>
<tbody>
<tr>
<td>Steel</td>
<td>205</td>
<td>7.87</td>
</tr>
<tr>
<td>aluminium</td>
<td>70</td>
<td>2.7</td>
</tr>
<tr>
<td>Titanium alloy</td>
<td>110</td>
<td>4.5</td>
</tr>
<tr>
<td>(Ti4% Al4% Mn)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>glass</td>
<td>70</td>
<td>2.5</td>
</tr>
<tr>
<td>nylon</td>
<td>2.8</td>
<td>1.1</td>
</tr>
<tr>
<td>polycarbonate</td>
<td>2.3</td>
<td>0.9</td>
</tr>
<tr>
<td>cement</td>
<td>25</td>
<td>2.6</td>
</tr>
<tr>
<td>alumina</td>
<td>400</td>
<td>3.98</td>
</tr>
<tr>
<td>Titania</td>
<td>200</td>
<td>4.1</td>
</tr>
<tr>
<td>YBCO</td>
<td>180</td>
<td>6.2</td>
</tr>
<tr>
<td>Zirconia</td>
<td>200</td>
<td>6.0</td>
</tr>
<tr>
<td>Diamond</td>
<td>1200</td>
<td>3.51</td>
</tr>
</tbody>
</table>
Force-Distance-Curve

Compressive force

Restoring Force

Restoring Force

Tensile force

Linear elastic region (Hooke's Law)

$F_{\text{max}}$

$2F_{\text{max}}$

$r_0$

$r_{\text{fail}}$

$r$

$S_0$

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The Theoretic Strength of Solids

- simple approximation -

assuming that generally bonds in solids fail at 25% elongation, which calculates to $1.25 \times r_0$.

$$S_0 \approx \frac{2F_{\text{max}}}{r_{\text{Bruch}} - r_0} \approx \frac{2F_{\text{max}}}{1.25r_0 - r_0}$$

The (tensile) strength of an ionic bonded solid should be $\sim \frac{1}{8}$ of the elastic modulus.
The Theoretic Strength of Solids
- more sophisticated approximation -

\[ E_{\text{bond}} = \frac{C}{r^n} - \frac{D}{r^m} \] generalized form of the potential – distance function

with \( n > m \) and \( \sigma_{\text{max}} \gg F_{\text{max}}/(r_0)^2 \)

\[ \sigma_{\text{max}} = \frac{E}{[(n+1)/(m+1)]^{(m+1)/(n-m)} \frac{1}{n+1}} \]

typical values for \( n \) and \( m \), in case of ionic bonds \( n = 9, m = 1 \) leads to

\[ \sigma_{\text{max}} \approx \frac{E}{15} \]

The (tensile) strength of an ionic bonded solid should be \( \sim 1/15 \) of the elastic modulus.
The Theoretic Strength of Solids

The tensile strength of ionic bonded solids should be about \(~ 1/10\) of the elastic modulus \(E\).

However, we find experimentally that the strength of these materials is about \(1/100\) to \(1/1000 \times E\). That is much less than our approach using the potential well predicts!!!

There must be other issues determining the low strength than the potential well!

Examples:
- \(\text{Al}_2\text{O}_3\): \(\sigma_{\text{bend}} = 330\) MPa, \(E = 300\) GPa (/ 910) (http://www.accuratus.com/)
- \(\text{SiC}\): \(\sigma_{\text{bend}} = 550\) MPa, \(E = 410\) GPa (/ 745)
- \(\text{BN}\): \(\sigma_{\text{bend}} = 75.8\) MPa, \(E = 46.9\) GPa (/ 620)
Summary

1.) the bond energy / force determines many physical properties of a solid, i.e. melting temperature $T_m$, thermal expansion $a$, elastic modulus $E$, theoretical strength $\sigma$.

2.) the deeper the potential well, the stronger the bonds, the higher the melting temperature. Covalency in ionic bonds stabilizes discrete structure elements, lowers melting temperature lower.

3.) the thermal expansion anharmonic potential well. Deeper potential well leads to smaller thermal expansion. Loose packed structures also result in smaller thermal expansion.

4.) stiffness / elastic modulus proportional to the curvature of the potential. Solids with stronger bonds are stiffer than solids with weaker bonds.

5.) theoretical strength should be ~1/10 of the elastic modulus $E$. However, experimentally measured strength values are about 1/100 to 1/1000 of this value.
Additional Slides
Ratio of the Bond Energy of Al\textsubscript{2}O\textsubscript{3} to MgO

\[ E_{bond} = \frac{z_1 \cdot z_2 \cdot e^2}{4\pi\varepsilon_0 \cdot r_0} \left( 1 - \frac{1}{n} \right) \]

\[ \frac{E_{Al\textsubscript{2}O\textsubscript{3}}}{E_{MgO}} = \left[ \frac{z_1 \cdot z_2}{r_0} \right]_{Al\textsubscript{2}O\textsubscript{3}} = 1.64 \]

Al\textsubscript{2}O\textsubscript{3}: \( r_0 = 193.5 \text{ pm}, \ n = 7 \)

MgO: \( r_0 = 212 \text{ pm}, \ n = 7 \)
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**Ratio of the Lattice Energy of Al\(_2\)O\(_3\) to MgO**

\[
E_{Lattice} = N_{Av} \cdot \frac{z_1 \cdot z_2 \cdot e^2}{4 \pi \varepsilon_0 \cdot r_0} \left(1 - \frac{1}{n}\right) \cdot \alpha
\]

\[
\frac{E_{Al_2O_3}^{Lattice}}{E_{MgO}^{Lattice}} = \frac{N_{Av} \cdot E_{bond}^{Al_2O_3}}{N_{Av} \cdot E_{bond}^{MgO}} \cdot \frac{\alpha^{Al_2O_3}}{\alpha^{MgO}} = 23.54
\]

\[
\frac{E_{bond}^{Al_2O_3}}{E_{bond}^{MgO}} = 1.64
\]

Al\(_2\)O\(_3\): \(\alpha^{Al_2O_3} = 25.0312\)

MgO: \(\alpha^{MgO} = 1.7475\)
Determination of „B“ (Born Constant) and „n“ Born Exponent

• at equilibrium
\[
\left( \frac{\partial E_{\text{lattice}}}{\partial r} \right)_{r=r_0} = 0
\]
\[r_0\] can be measured

\[
- \frac{N_{\text{Av}} \cdot z_1 \cdot z_2 \cdot e^2 \cdot \alpha}{4\pi\varepsilon_0 \cdot r_0^2} - \frac{n \cdot B}{r_0^{n+1}} = 0
\]

\[B = -\frac{N_{\text{Av}} \cdot z_1 \cdot z_2 \cdot e^2 \cdot \alpha \cdot r_0^{n+1}}{4\pi\varepsilon_0 \cdot r_0^2 \cdot n}
\]

\[B = -\frac{N_{\text{Av}} \cdot z_1 \cdot z_2 \cdot e^2 \cdot \alpha \cdot r_0^{n-2}}{4\pi\varepsilon_0 \cdot n}
\]

• n is still unknown!

• To find n, we need to move away from equilibrium, i.e. compress the solid and measure its compressibility
Compressibility

- compressibility is measured
- then we can calculate $n$

$\kappa = -\frac{1}{V_0} \cdot \left[ \frac{\partial V}{\partial P} \right]_T$

$$\kappa = \frac{(4\pi \varepsilon_0) \cdot 18r_0^4}{\alpha \cdot e^2 \cdot (n - 1)}$$

- Examples: NaCl $4.18 \times 10^{-11}$ 1/Pa -> $n = 7.7$
Sample calculation for NaCl

\[ \varepsilon = 8.854 \times 10^{-12} \text{ SI units} \]
\[ e = 1.602 \times 10^{-19} \text{ coulombs} \]
\[ \alpha = 1.74756 \text{ (NaCl structure)} \]
\[ d = 5.628 \times 10^{-10} \text{ m giving } r_0 = 2.814 \times 10^{-10} \text{ m} \]
\[ \kappa = 4.18 \times 10^{-11} \text{ SI} \]

\( n \) is found by

\[ n = 1 + \frac{(4\pi\delta)(18r_0^4)}{Me^2\kappa} = 1 + \frac{4(3.14159)(8.854 \times 10^{-12})(18)(2.814 \times 10^{-10})}{(1.74756)(1.602 \times 10^{-19})^2(4.18 \times 10^{-11})} = 7.70 \]

\[ E_{\text{lat}} = \frac{N_0MZ^+Z^-e^2}{4\pi\delta r_0} \left(1 - \frac{1}{n}\right) = \frac{(6.022 \times 10^{23})(1.74756)(+1)(-1)(1.602 \times 10^{-19})^2}{(4)(3.14159)(8.854 \times 10^{-12})(2.814 \times 10^{-10})} \left(1 - \frac{1}{7.70}\right) \]

\[ = -750.6 \text{ kJ/mol} \]

This compares to 769.4 kJ/mole experimental (2.4% error)