

Lecture 18: 11.09.05 Binary systems: miscibility gaps and eutectics

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Reading:

[Lupis, Chemical Thermodynamics of Materials, Ch VII, 'Binary Phase Diagrams,' pp. 204-219

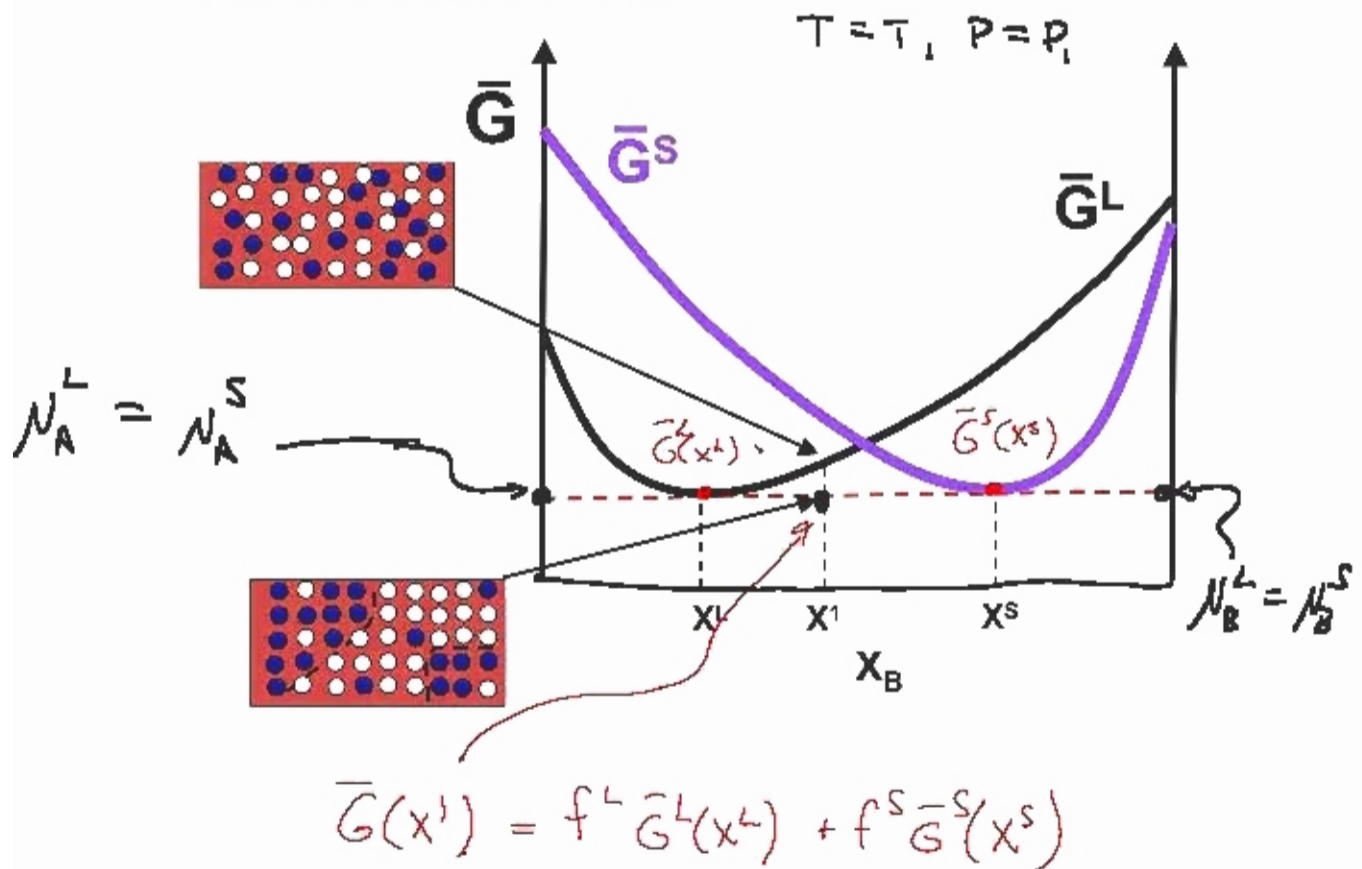
Supplementary Reading:

Last time

Free energy and phase diagrams of ideal binary solutions

Key points:

1. Common tangents to free energy curves define composition regions where phase separation (two-phase equilibria) occurs.
2. Phase separation lowers the overall free energy by splitting the homogeneous system into a weighted mix of two separate phases, which each have lower free energy than the starting homogeneous phase.
3. Compositions of the phases in two-phase regions are given by the tangent points, and the amount of each phase is determined by the lever rule.



- Two-phase equilibrium introduces the phase fraction, determined by the lever rule:

$$f^S = \text{mole fraction solid in whole system} = \frac{n_A^S + n_B^S}{n_A + n_B} = \frac{X^1 - X^L}{X^S - X^L}$$

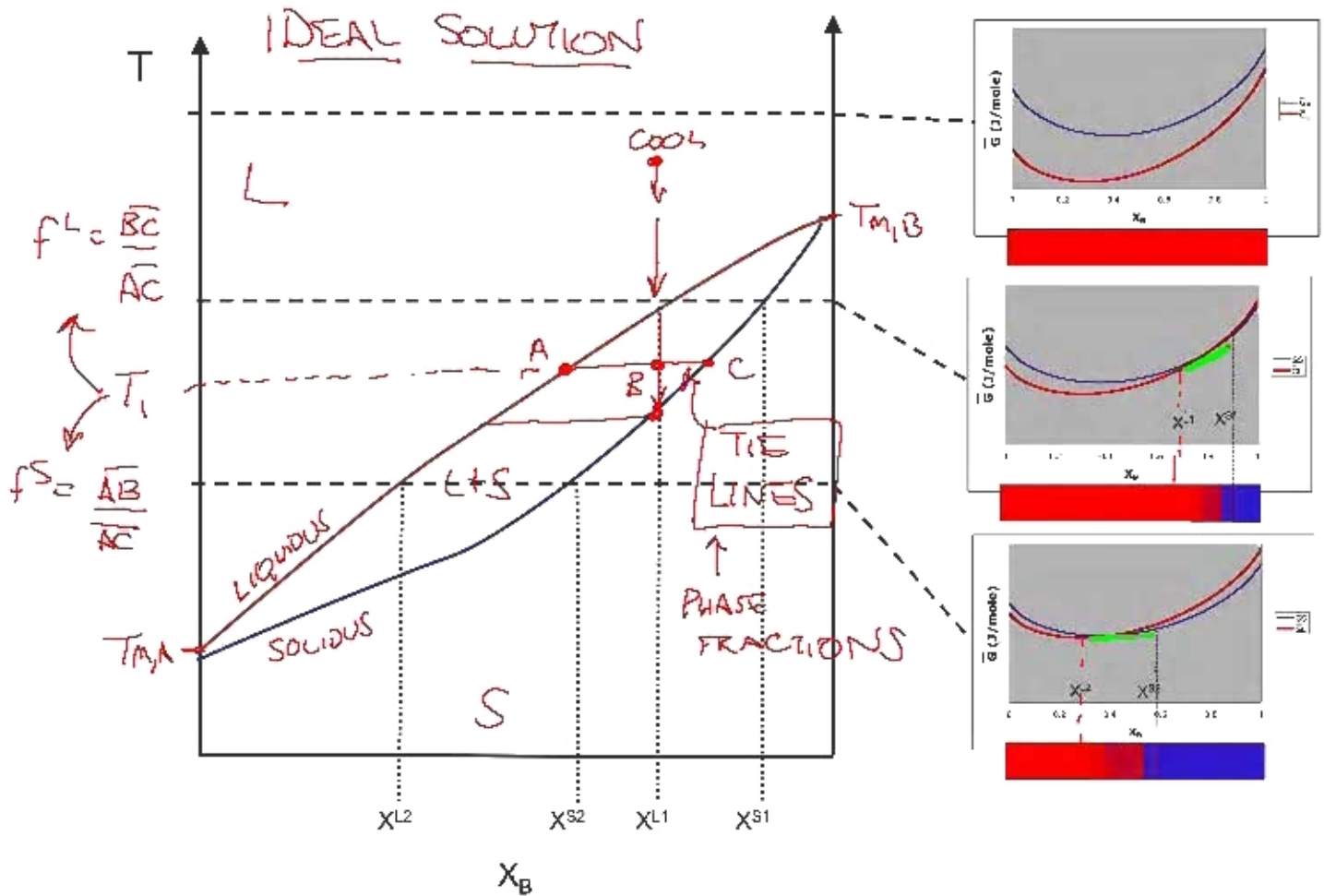
$$f^L = \text{mole fraction liquid in whole system} = \frac{n_A^L + n_B^L}{n_A + n_B} = \frac{X^S - X^1}{X^S - X^L}$$

$$f^S + f^L = 1$$

- Free energy diagrams directly relate to binary phase diagrams:

Key points:

- Free energy diagrams define the structure of the phase diagram.
- Compositions of two-phase regions, which are tangent points on the free energy diagram, become phase boundaries on the phase diagram.
- The lever rule is directly applied to tie lines on the phase diagram, to determine the amount of each phase present in two-phase regions.

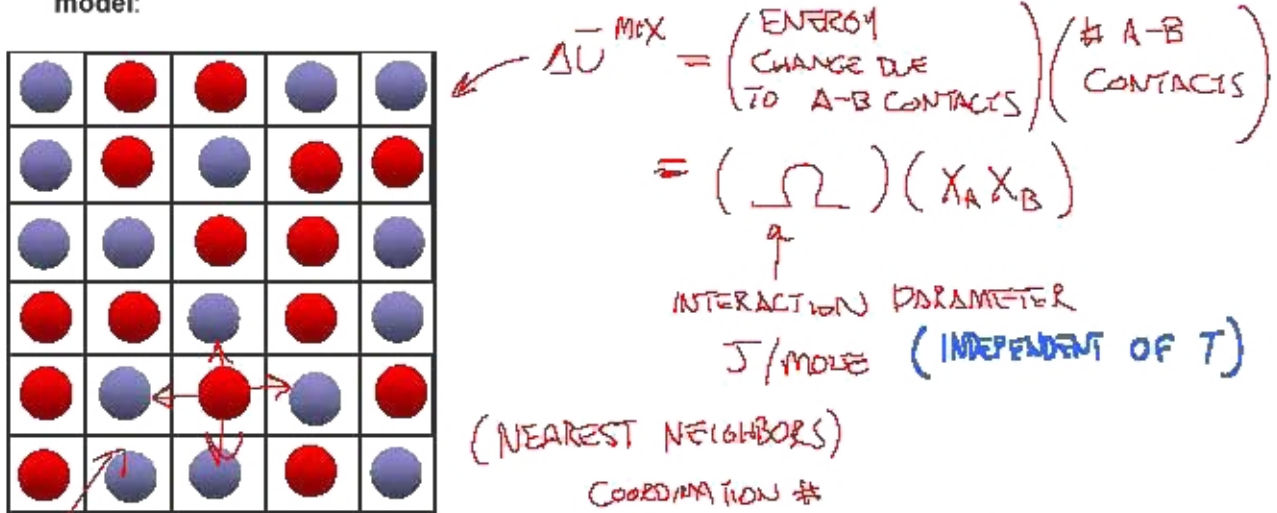


- The ideal solution is a special case- not all materials form binary solutions that are miscible at all compositions and all temperatures, particularly in the solid state. Materials that have incompatible crystal structures cannot form homogeneous solid solutions- they are forced to phase separate into an A-rich solid phase and a B-rich solid phase, to preserve their stable crystalline forms. Today we will examine the phase diagrams of these and other common binary materials systems.

Binary solutions with limited miscibility in the solid state: Miscibility gaps

The Regular Solution Model, part I

- What happens if the molecules in the solution interact with a finite energy? The enthalpy of mixing will now have a finite value, either favoring ($\Delta\bar{H}^{mix} < 0$) or disfavoring ($\Delta\bar{H}^{mix} > 0$) mixing of the two components. The simplest model of a solution with finite interactions is called the **regular solution model**:



PROBABILITY OF AN A-B CONTACT: $X_A \left[\left(\frac{z}{2} \right) X_B \right]$

$\left[\begin{matrix} < 0 & \text{FAVORABLE MIXING} \\ > 0 & \text{UNFAVORABLE MIXING} \end{matrix} \right]$

- Let the enthalpy of mixing take on a finite value given by:

$$\Delta\bar{H}^{mix} = \Delta\bar{U}^{mix} + P\Delta\bar{V}^{mix} \approx \Delta\bar{U}^{mix}$$

(P IS FIXED) USUALLY SMALL

$$\Delta\bar{H}^{mix,RS} = \Omega X_A X_B$$

- We take the entropy of mixing to be the same as in the ideal solution. This gives a total free energy of mixing which is:

$$\Delta\bar{G}^{mix,RS} = \Delta\bar{H}^{mix,RS} - T \Delta\bar{S}^{mix,RS} = \Omega X_A X_B + RT [X_A \ln X_A + X_B \ln X_B]$$

$\Delta\bar{S}^{mix,RS} = \Delta\bar{S}^{mix,IDEAL}$

- We can also use the equations above to determine the enthalpy, entropy, and Gibbs free energy of the regular solution:

$$\Delta \bar{G}^{mix,rs} = \bar{G}^{rs} - \bar{G}^{unmixed}$$

$$\bar{G}^{rs} = \Delta \bar{G}^{mix,rs} + \bar{G}^{unmixed} = \Omega X_A X_B + RT[X_A \ln X_A + X_B \ln X_B] + \mu_A^o X_A + \mu_B^o X_B$$

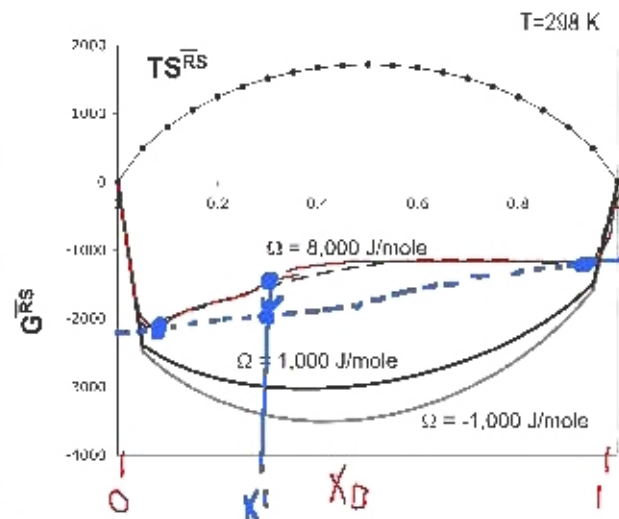
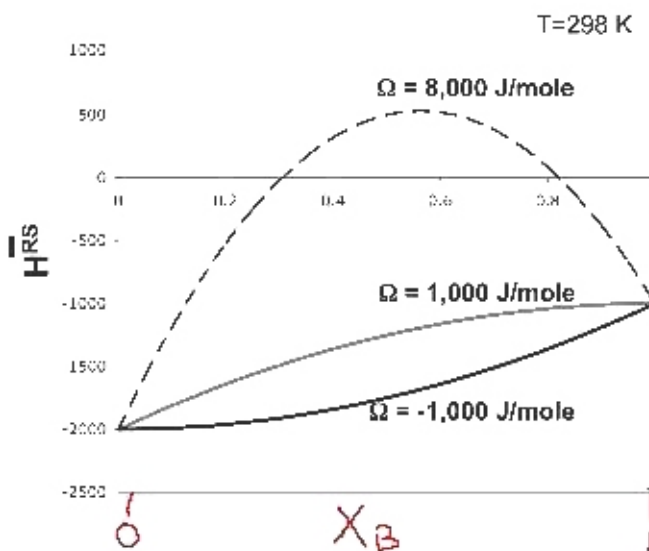
$$\bar{S}^{rs} = - \left(\frac{\partial \bar{G}^{rs}}{\partial T} \right)_{P,n} = -R[X_A \ln X_A + X_B \ln X_B]$$

$$\bar{H}^{rs} = \bar{G}^{rs} + T\bar{S}^{rs} = \Omega X_A X_B + \mu_A^o X_A + \mu_B^o X_B$$

- The regular solution model describes the liquid phase of many real systems such as Pb-Sn, Ga-Sb, and Ti-Sn, and some solid solutions. Today we will analyze the behavior of a system with this free energy function; in a few lectures we will show how the given forms of the enthalpy and entropy of mixing arise from consideration of molecular states (using statistical mechanics).
- Let's look at the behavior of regular solutions graphically. The plots below are all prepared for a binary system where the standard state chemical potentials are assumed to be approximately invariant with temperature (i.e., the endpoints of the free energy curves are not moving with temperature- approximately valid over certain temp. ranges for some solids):

$$\mu_A^o = -2,000 \frac{J}{mole}$$

$$\mu_B^o = -1,000 \frac{J}{mole}$$

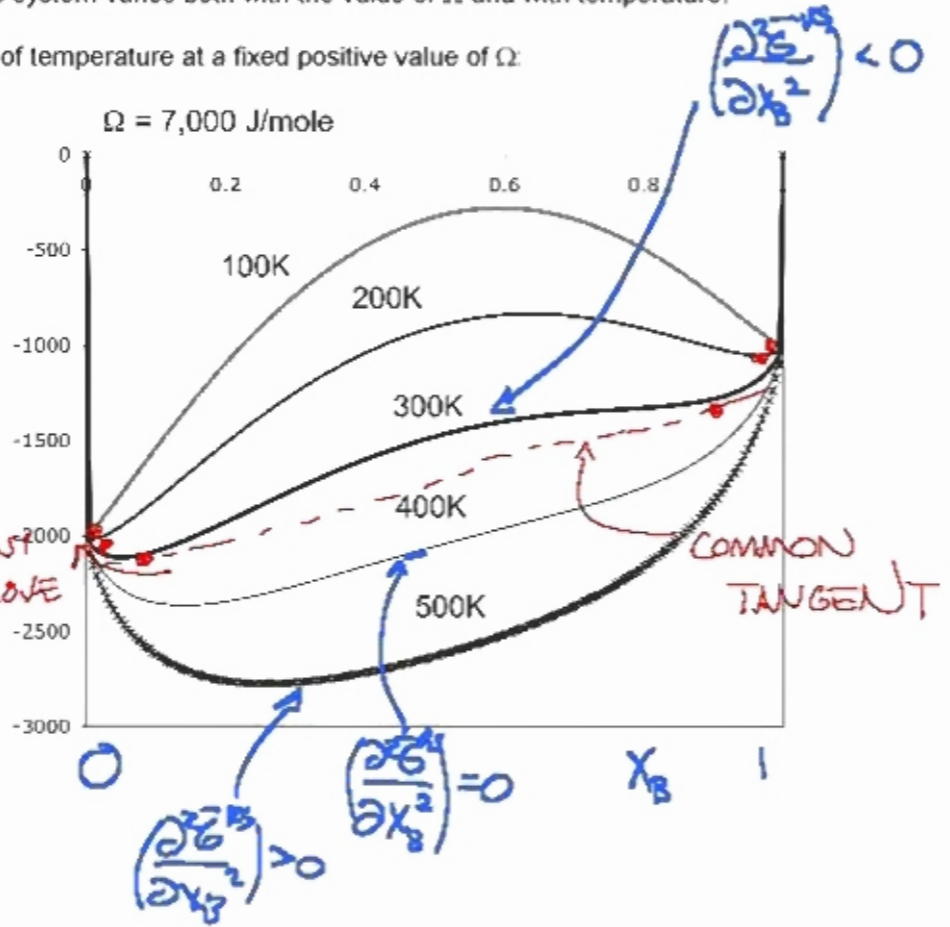


- The free energy of the system varies both with the value of Ω and with temperature:
 - As a function of temperature at a fixed positive value of Ω :

$$\bar{G}^{RS} = \bar{H}^{RS} - T \bar{S}^{RS}$$

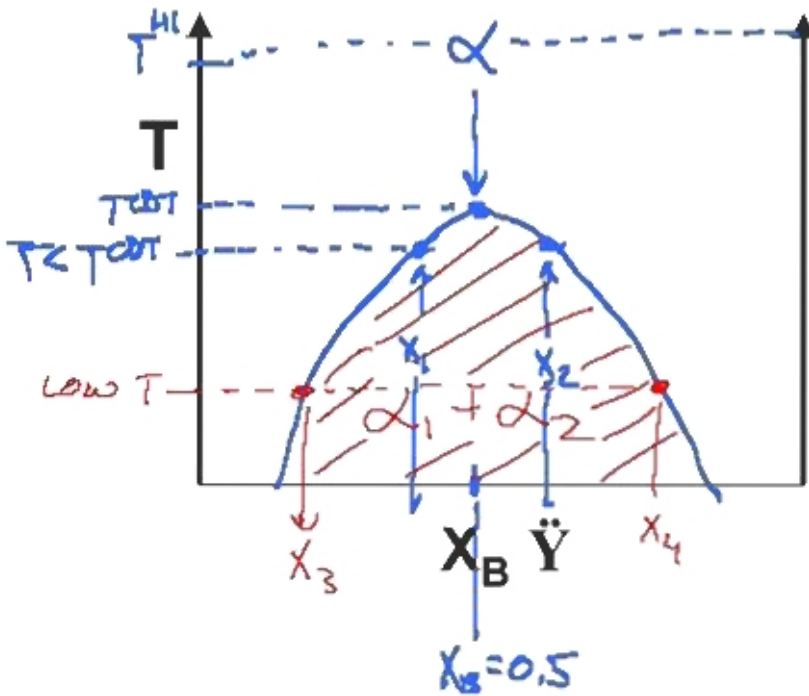
↑
Favors
Mixing

COMMON TANGENT
ENDPOINTS MOVE
TOWARD $X_B = 0$
AND $X_B = 1$ AXES



Phase diagram of a regular solution

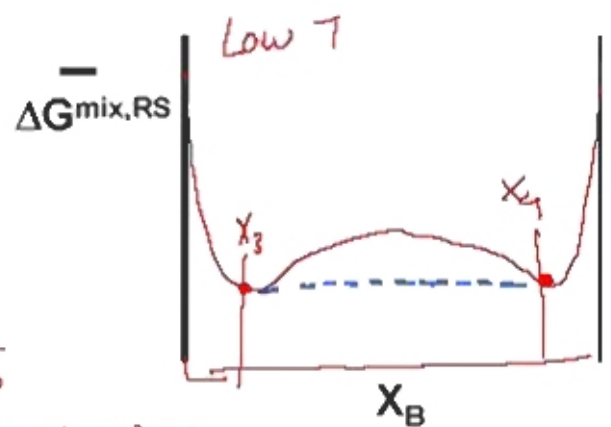
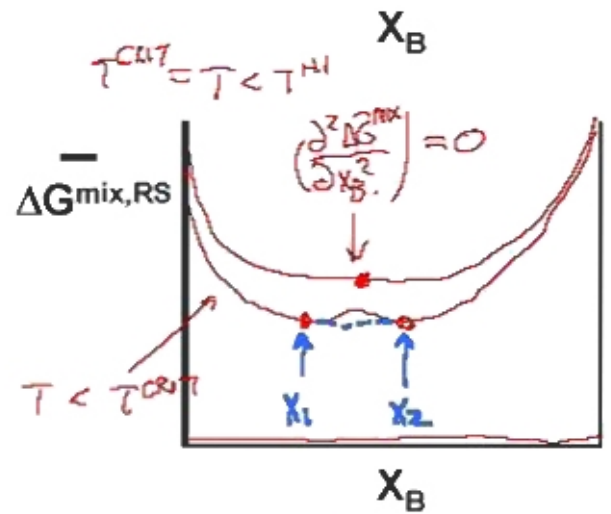
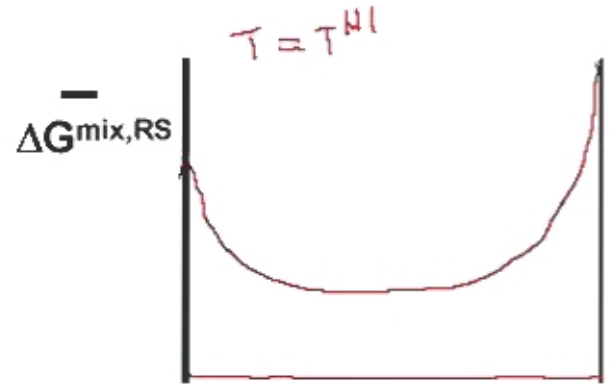
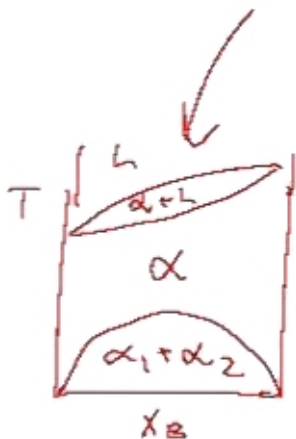
$\bar{G}^{RS} \rightarrow$ SOLID PHASE α



MISCIBILITY GAP

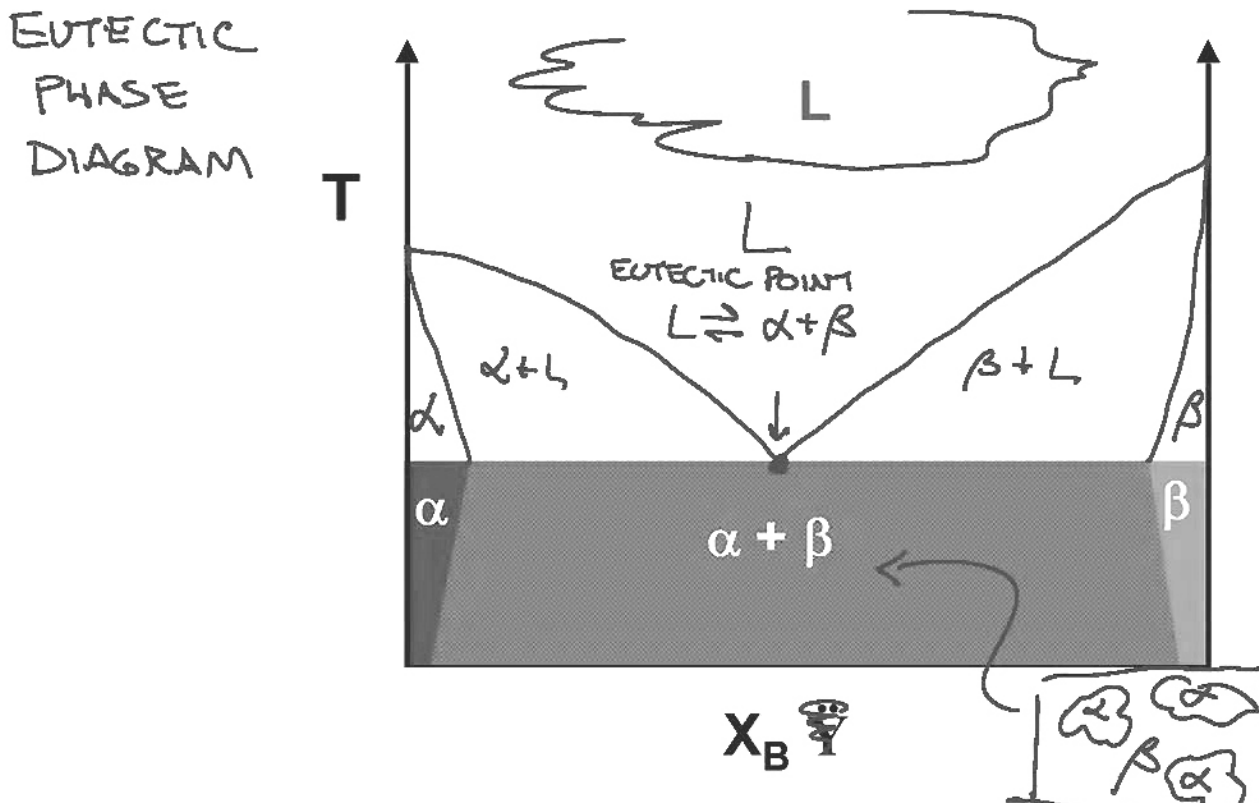
\rightarrow SOLIDS OR LIQUIDS

$\rightarrow \alpha_1, \alpha_2$ HAVE SAME STRUCTURES BUT CHEMICALLY INCOMPATIBLE



Eutectic systems

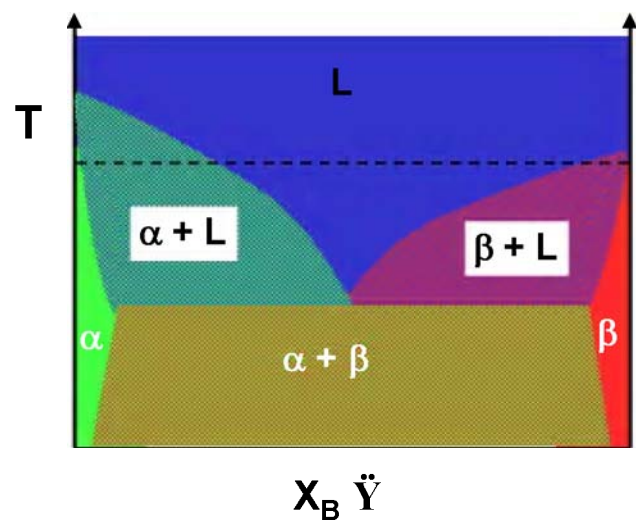
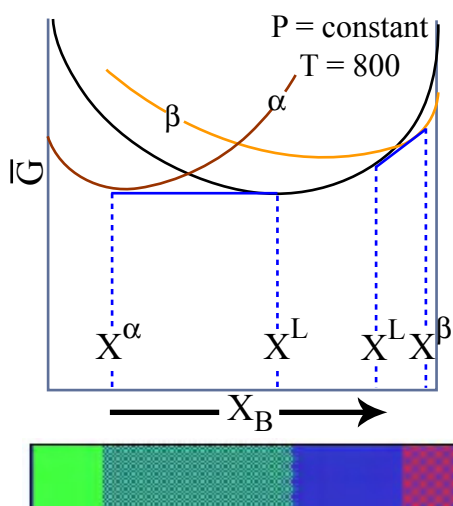
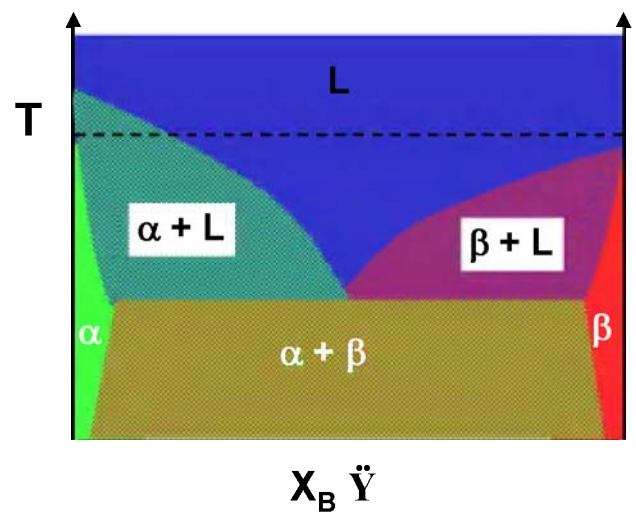
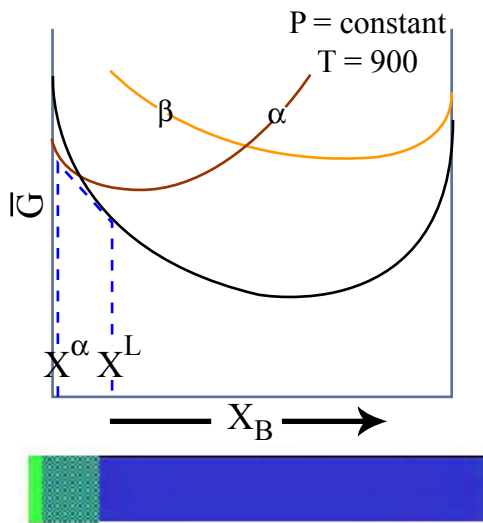
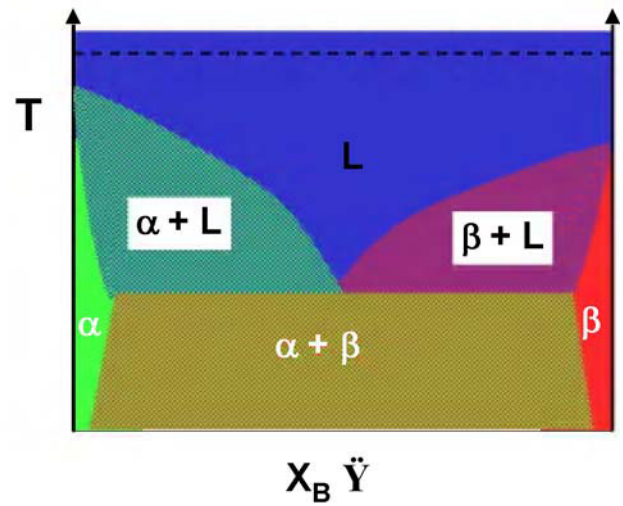
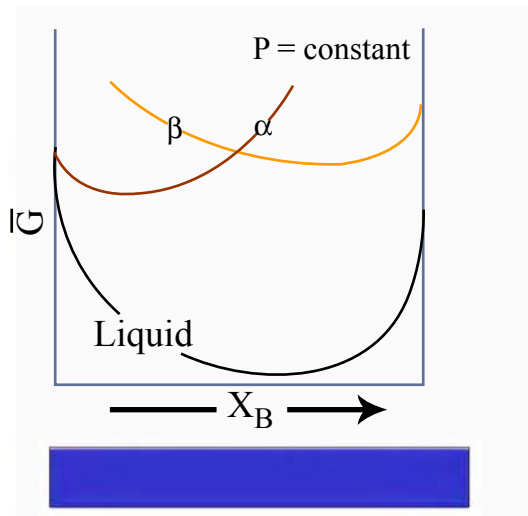
- It is commonly found that many materials are highly miscible in the liquid state, but have very limited mutual miscibility in the solid state. Thus much of the phase diagram at low temperatures is dominated by a 2-phase field of two different solid structures- one that is highly enriched in component A (the α phase) and one that is highly enriched in component B (the β phase). These binary systems, with unlimited liquid state miscibility and low or negligible solid state miscibility, are referred to as **eutectic systems**.
 - The behavior just described, where the two components are completely miscible at high temperatures in the liquid state and phase-separated into two solids at low temperatures would be represented by a phase diagram as follows:



- Now the question is, what happens in the region between high and low temperatures?
- Let's examine how the phase diagram of a eutectic system develops.

Free energy diagrams of eutectic systems

- Suppose we have a binary solution of A and B. The molar free energy for each phase can be diagrammed for as a function of composition, as we did for the simple ideal solution:(1)



Graphs by MIT OCW.

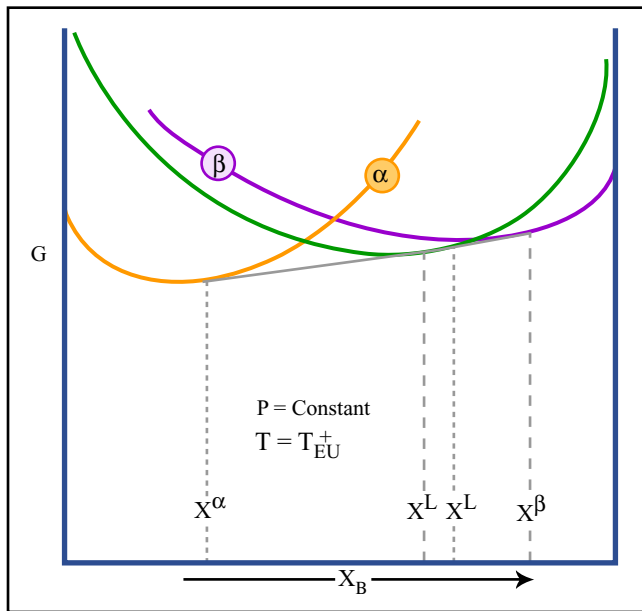
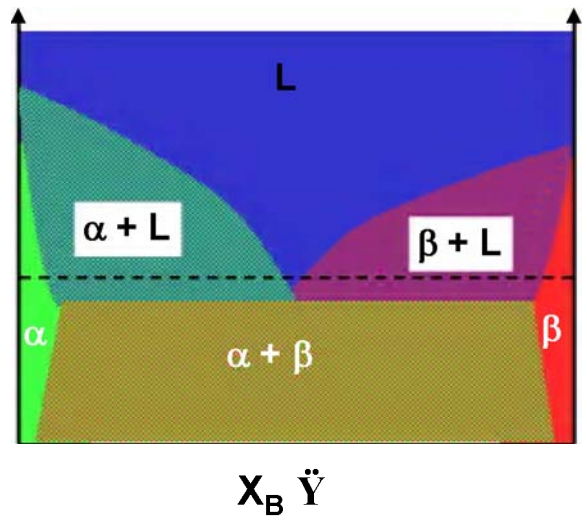
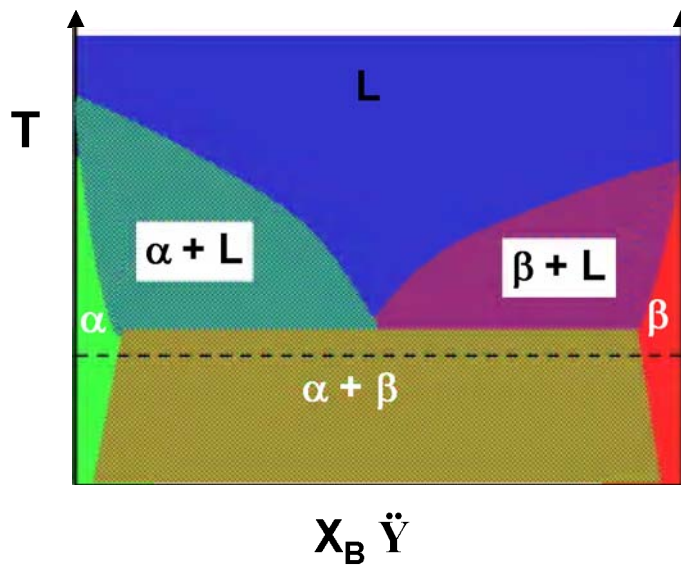
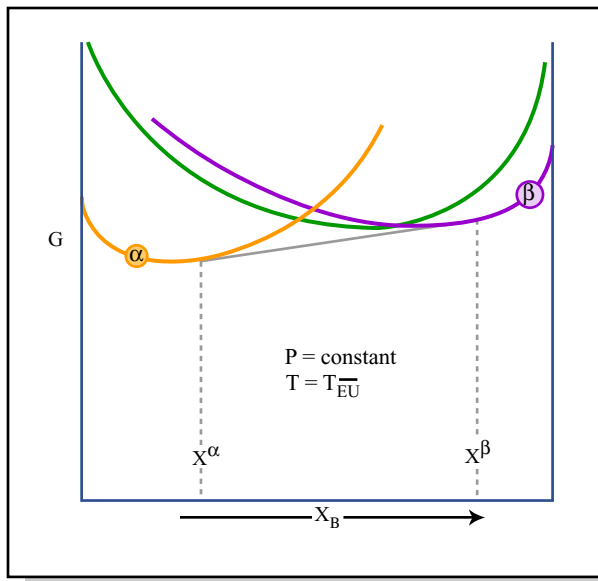


Figure by MIT OCW.

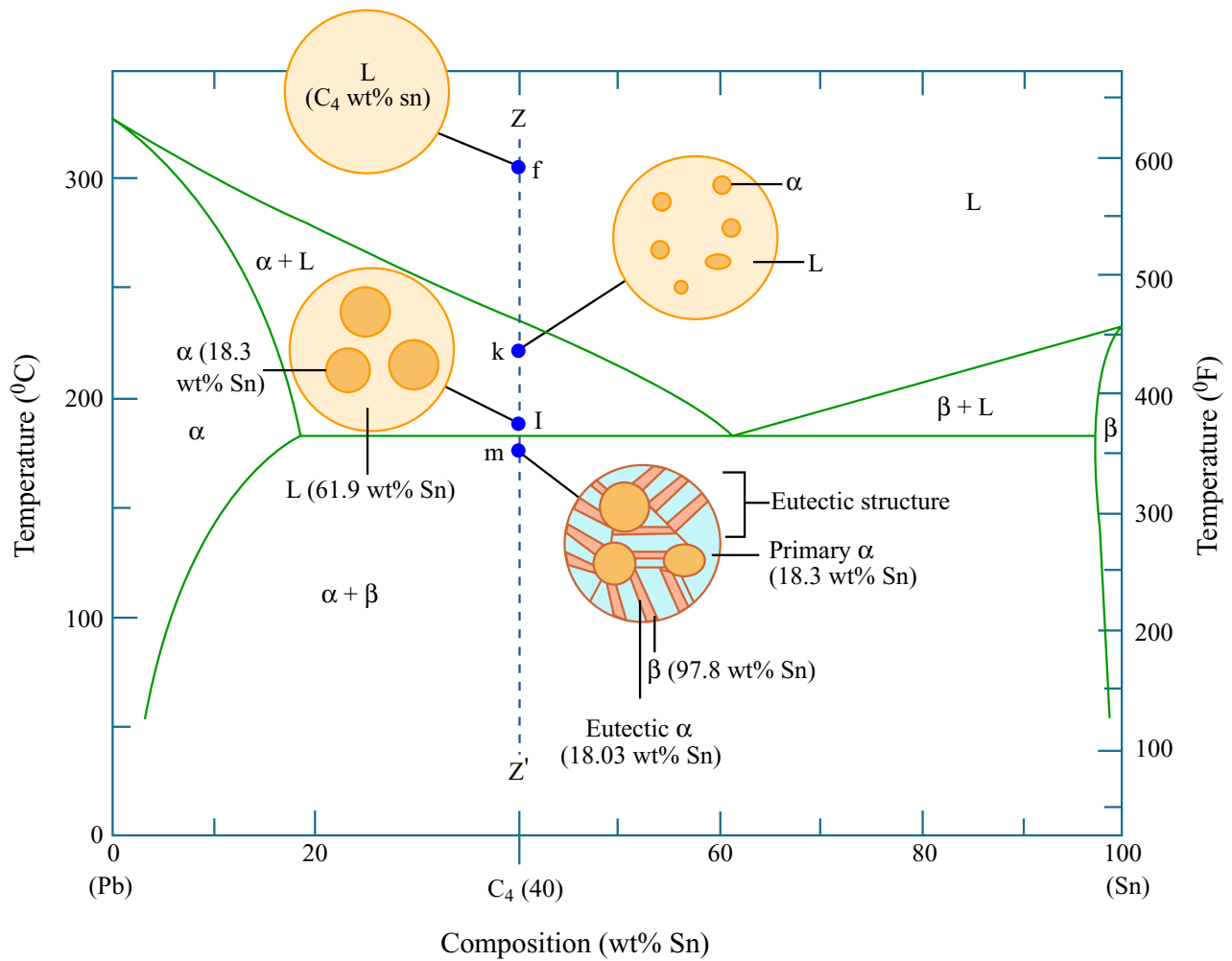




(© W.C. Carter 2002, p. 203)

Analyzing phase equilibria on eutectic phase diagrams

- Next term, you will learn how these thermodynamic phase equilibria intersect with the development of **microstructure** in materials:



Schematic representations of the equilibrium microstructures for a lead-tin alloy of composition C_4 as it is cooled from the liquid-phase region.

Figure by MIT OCW.

Example eutectic systems

Solid-state crystal structures of several eutectic systems			
Component A	Solid-state crystal	Component B	Solid-state crystal

	structure A		structure B
Bi	rhombohedral	Sn	tetragonal
Ag	FCC (lattice parameter: 4.09 Å at 298K)	Cu	FCC (lattice parameter: 3.61 Å at 298K)
Pb	FCC	Sn	tetragonal

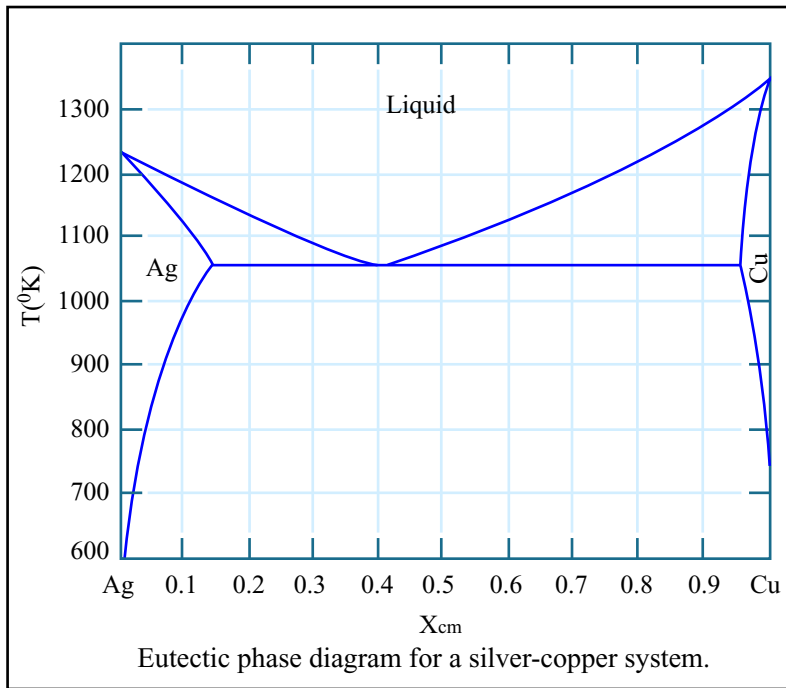


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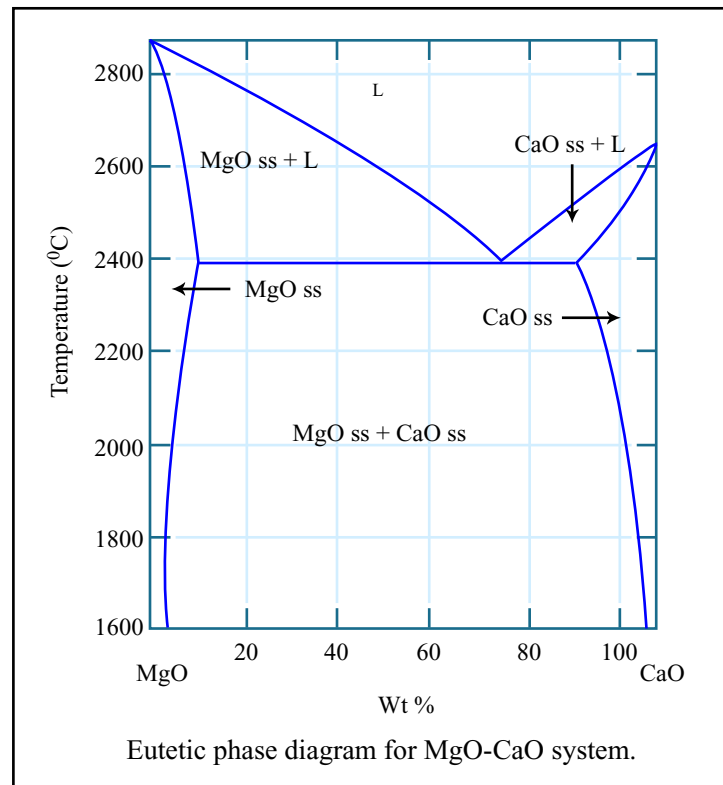


Figure by MIT OCW.

References

1. Carter, W. C. 2002. 3.00 Thermodynamics of Materials Lecture Notes.
2. McCallister, W. D. 2003. *Materials Science and Engineering: An Introduction*. John Wiley & Sons, Inc., New York.
3. Lupis, C. H. P. 1983. *Chemical Thermodynamics of Materials*. Prentice-Hall, New York.
4. Bergeron, C. G., and S. H. Risbud. 1984. *Introduction to Phase Equilibria in Ceramics*. American Ceramic Society, Westerville, OH.