Solid State Synthesis - Aspects of Thermodynamic Control

Chem 462

September 28, 2004

Phase Rule

P + F = C + 2

- P = # of phases present at equilibrium
- C = # of components needed to describe the system
- F = # of degrees of freedom (# of thermodynamic variables - taken from T, P, compositions of components)

This "full" form of the phase rule is used when all three common physical states (*s*, *l*, *g*) are important.

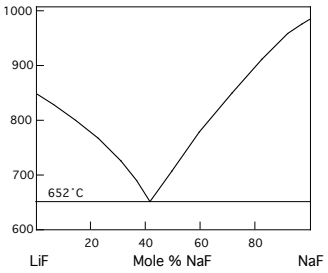
Condensed Phase Rule

P + F = C + 1 (instead of + 2)

- When the vapor pressure of all components is negligible, the effective number of degrees of freedom can be reduced by one.
- Pressure is not an important thermodynamic variable, leaving only two kinds variables necessary to describe the solid solution – temperature and compositions of the components.

A Boring diagram: LiF-NaF

Discuss the system in every region.



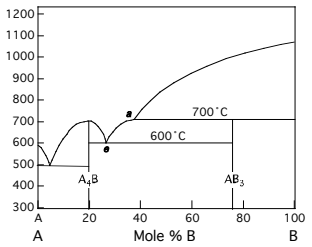
Hypothetical T-C diagram

A_4B - congruently melting - easily synthesized

e - eutectic point

a - peritectic point

AB_3 - how should it be synthesized?



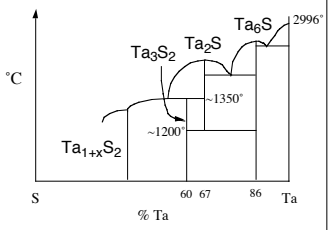
Ta-S system (Exam sample)

(a) What is likely to be the best way to prepare Ta_6S?

(b) What is likely to be the best way to prepare Ta_2S?

(c) What will occur (if anything) when a sample of Ta_2S is heated from 25 to 1100 ˚C?

(d) What is likely to be the best way to prepare Ta_3S_2? Explain.



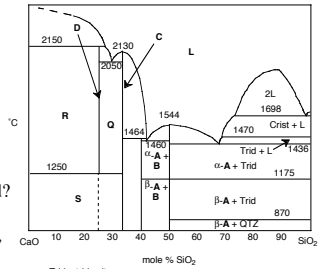
$CaO\text{-}SiO_2$ system

This is effectively a two-component system, even though there are three elements present. Why?

What are the congruently melting compounds?

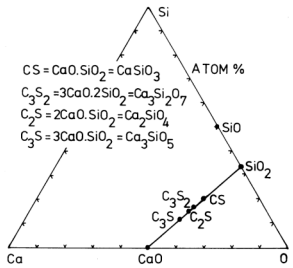
What is compound D and how might it be prepared?

Suggest structural features that may be present in A, C and D.



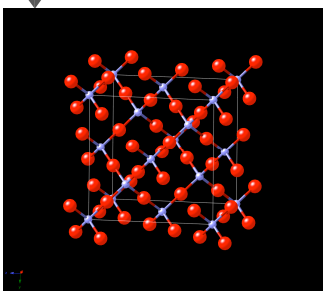
Trid = tridymite
Crist = cristobalite
QTZ = quartz

Ternary System Ca-Si-O



Binary join $CaO\text{-}SiO_2$ in the ternary system Ca-Si-O. Note the method used for labeling of phases, C = CaO, S = SiO_2. This type of abbreviation is widely used in oxide chemistry

SiO_2 - a Network structure



- Idealized (cubic) structure of cristobalite form of SiO_2.