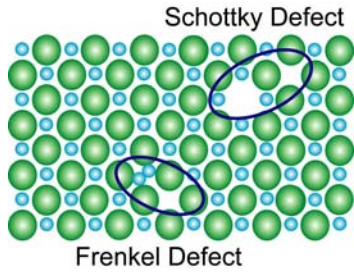


Class 3: Defects in Ceramics

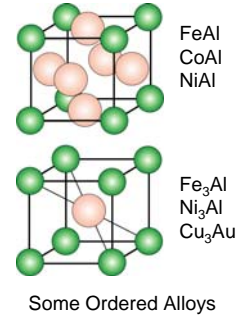


PRIME Modules
Project-based Resources for Introduction to Materials Engineering

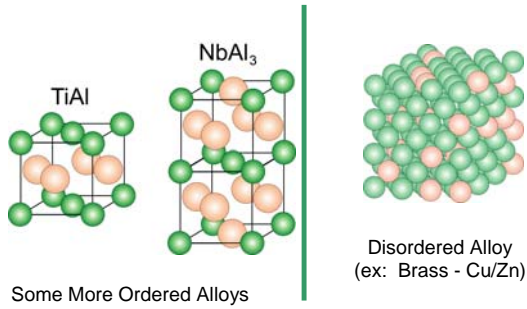
A solid solution is a single phase made up of 2 or more elements.

Alloys are mixtures of 2 or more elements.

When an element is added to another, the compound can either be one phase (form a solid solution) or form two phases.



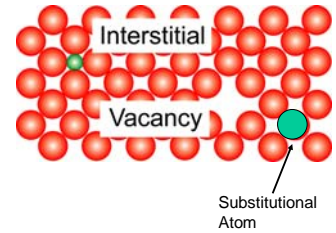
The single phase in a solid solution can be ordered or disordered



Point defects are defects in the crystal structure that occupy one spot.

In solid solutions, the added element(s) is incorporated in point defects

- There are three main types:
- (a) vacancies,
 - (b) interstitial atoms
 - (c) substitutional atoms.



The concentration of vacancies and interstitials increases with temperature

Vacancies and interstitials are always present in a solid. They provide entropy to the system, so they are thermodynamically stable.

The equation that describes the relationship between the number of vacancies (or interstitials) and temperature is:

$$N_v = N \exp\left(-\frac{Q_v}{kT}\right)$$

Temperature independent constant

Energy barrier

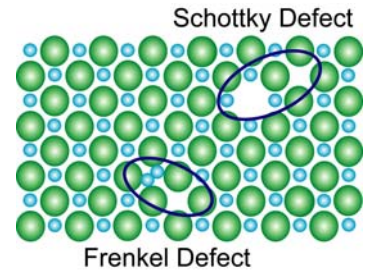
Boltzmann's constant

Schottky and Frenkel defects are defect pairs that exist in ceramics

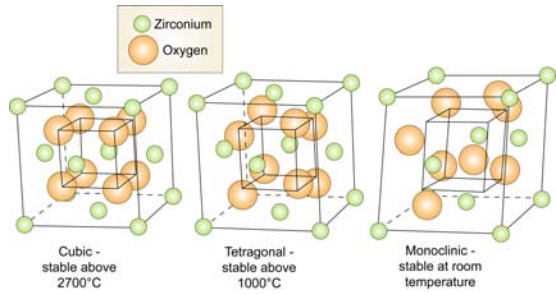
A Schottky defect is an anion and cation vacancy.

A Frenkel defect is a cation interstitial and a cation vacancy

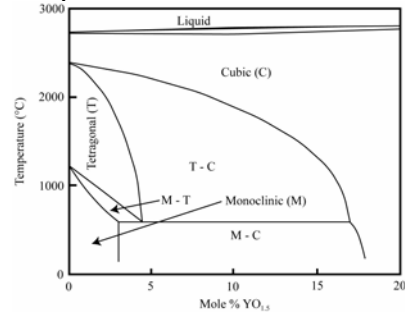
The defects occur in pairs because it is necessary to maintain charge neutrality.



Other defect clusters and pairs also exist in ceramics to maintain neutrality

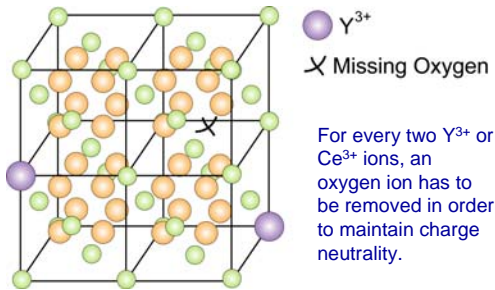


YO is added to ZrO₂ to stabilize it (make the cubic crystal structure stable at lower temperatures)



Cut of ZrO₂-YO Phase Diagram: H. G. Scott, Phase relations in the zirconia-yttria system, *Journal of Materials Science*, 10 [9] 1527-1535 (1975)

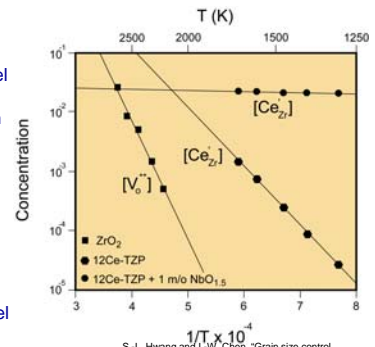
In SOFC, zirconia is doped with Y or Cs to stabilize the zirconia.



The defect concentration increases with temperature

For applications in fuel cells, ZrO₂ is commonly doped with yttrium or cerium, which results in oxygen vacancies.

The oxygen vacancy concentration increases as the temperature of the fuel cell increases



S.-L. Hwang and L.-W. Chen, "Grain size control of tetragonal zirconia polycrystals using the space charge concept," *Journal of the American Ceramic Society*, 73 [11] 3269-3277 (1990).

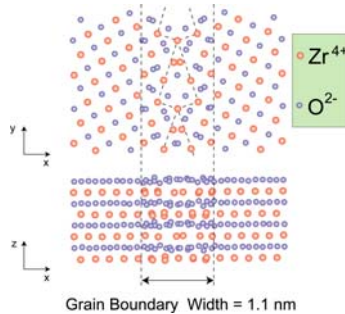
Defects that exist in 3D are called planar defects

Planar defects are also important in SOFC

External Surfaces - this is an obvious boundary, along which the crystal structure terminates.

Grain Boundaries are a boundary separating single crystals (called grains).

Twin Boundaries are a type of grain boundary where there is a special symmetry.

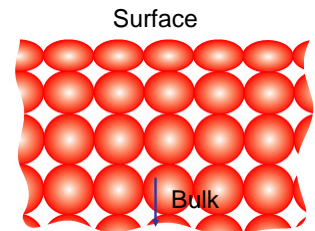


Surfaces can be thought of as a 3D defect

The atomic coordination at the surface is not fully comparable to the atoms within a crystal.

The surface atoms have neighbors on only one side; therefore they are less firmly bonded than the internal atoms.

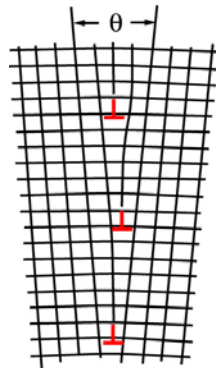
They have broken bonds which make them more reactive



Grain boundary results due to mismatch between neighboring grains

A low angle grain boundary has a small mismatch between grains that results in edge dislocations at the interface

Edge dislocations are a 2-D (line) defect. They are an extra half plane of atoms



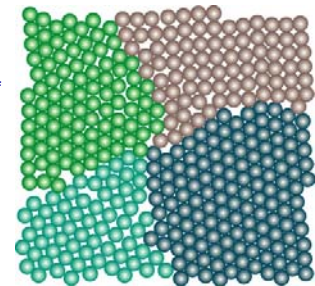
High Angle grain boundaries are when there is large mismatch between neighboring grains

Large disorder at the grain boundaries result in large gaps in the material

In spite of the disordered arrangement of atoms and lack of regular bonding at the boundaries, a polycrystalline materials is very strong.

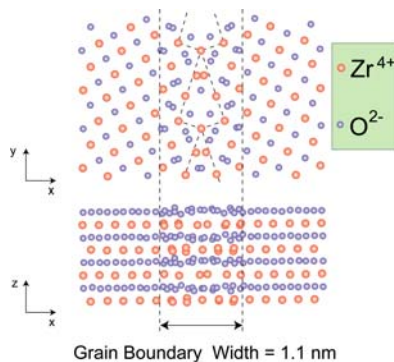
Cohesive forces within and across the boundary are present.

Furthermore, the density of a polycrystalline material is virtually identical to that of a single crystal of the same material.



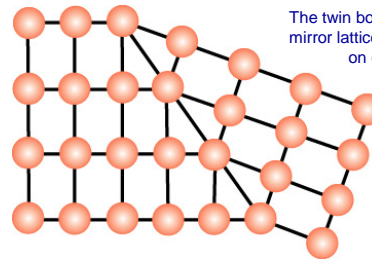
High Angle Grain Boundaries in Zirconia

Oxygen ions can move easily through the grain boundaries because of the extra spacing in between atoms.



C.A.J. Fisher and H. Matsubara, "Molecular dynamics investigation of grain boundary phenomena in cubic zirconia," *Computational Materials Science*, 14 (1999) 177-184.

Twin boundaries are 3 Defects with symmetry across the interface



The twin boundary has a specific mirror lattice symmetry. Atoms on one side of the boundary are located in mirror image positions of the atoms on the other side. Twinning occurs on a definite crystallographic plane and in a specific direction, both of which depend on the crystal structure.

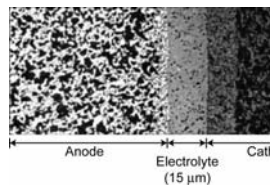
W.D. Callister, *Materials Science and Engineering An Introduction 5/e*, (John Wiley and Sons, New York, 2000).

Nanocrystals are materials with small grains and many grain boundaries

Nanocrystalline materials do not constitute a distinct class of materials. They are simply materials that have a very small grain size (i.e. lots of grain boundary area).

Because of their small grain size, they can have unique properties.

In particular, forming of these materials into useful components can be easier compared to microcrystalline materials. Hence, the preferred use of these materials for SOFC manufacturing.



F. Tietz, H.-P. Buchkremer, and D. Stöver, "Components manufacturing for solid oxide fuel cells," *Solid State Ionics*, 152-153 (2002) 373-381.

In summary: A "real" crystal has many different kind of defects in it

Crystals contain point, line, and planar defects

In ceramics, point defects exist in pairs or clusters to maintain neutrality

Defect concentrations increase with temperature

