IMPERFECTION IN CERAMICS

Are defect in ceramic different??

- Ceramics contain charged defects; metals cannot

- Ceramics vs FCC metal crystals (Cu):
  - The concentration of impurities in ceramics is usually much greater than that of intrinsic defects.
  - Dislocations are usually much less important for deformation mechanisms than they are in metals.
  - Surfaces and interfaces are even more important for ceramics
  - Pores and voids are often very much more important for ceramics.

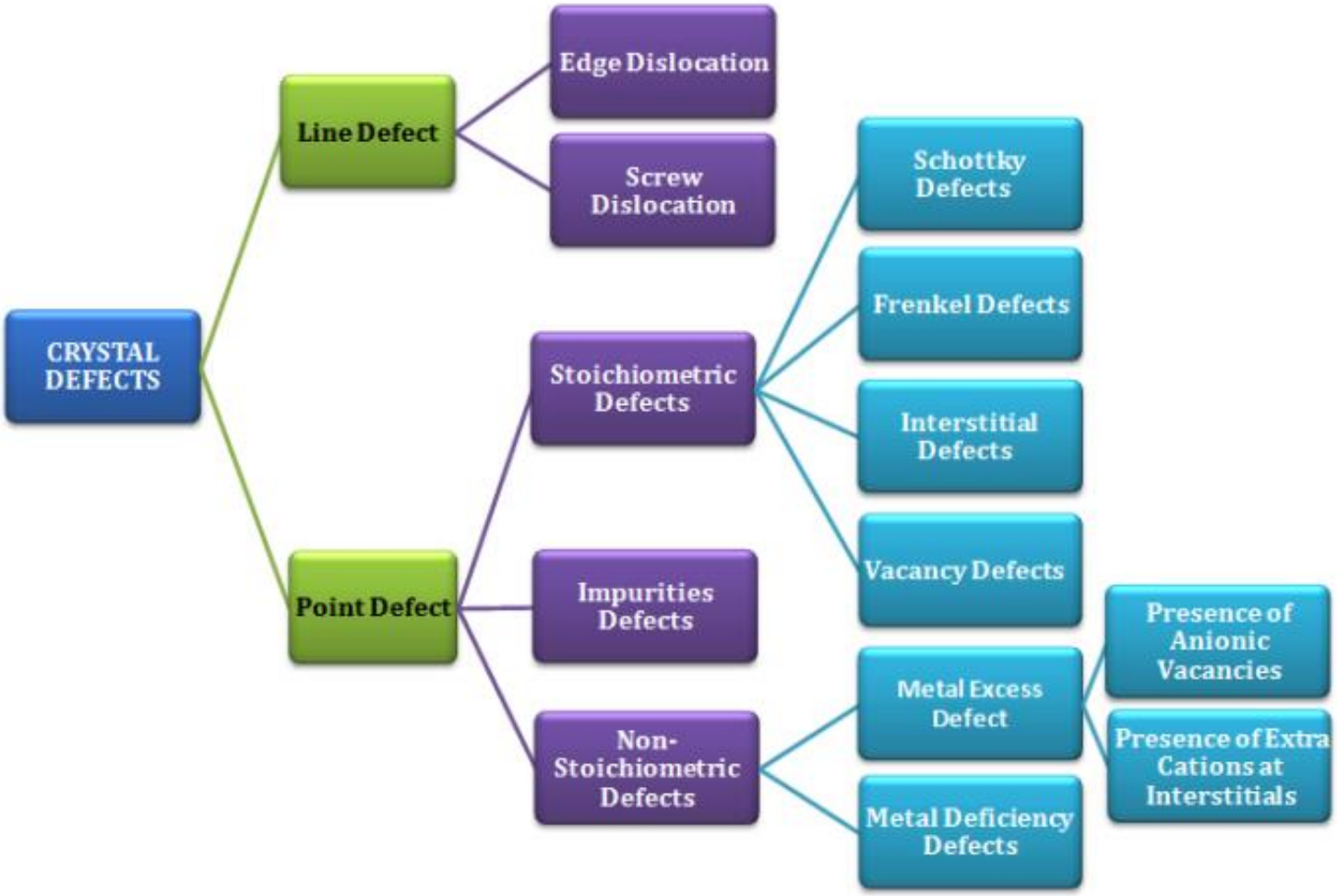
- processing ceramics often meant trying to remove pores and voids during sintering because they weakened the final material

- interested in highly porous ceramics
  - very large surface area
  - application as catalysts, catalyst supports, or filters.

Types of point defect

- Defect hierarchy

Dimension	Name	Example
Zero	Point Defect	Vacancy Impurities a) Interstitial atoms b) Substitutional atoms
One	Line Defect	Dislocation
Two	Planar/area defect	Grain Boundary
Three	volume defect	Pore crack



- **Stoichiometric Defects**

It is a type of point defects which does not disturb the stoichiometry of solid. This is also known as Intrinsic or Thermodynamic Defects.

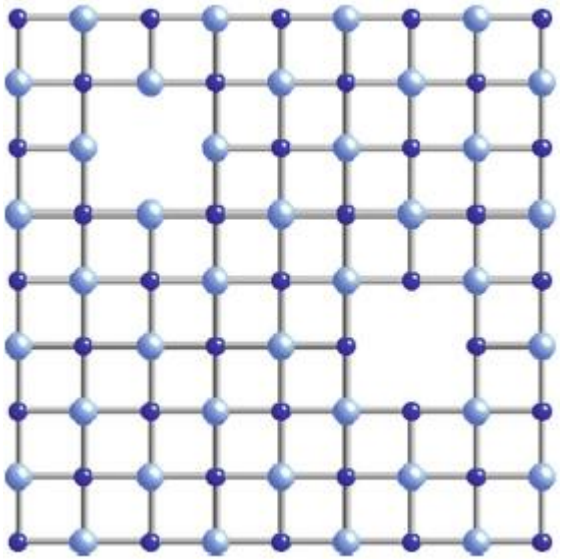
- **Non-Stoichiometric Defects**

There are large numbers of inorganic solids found which contain the constituent particles in non-stoichiometric ratio because of defects in their crystal structure.

Types of point defect

Vacancies

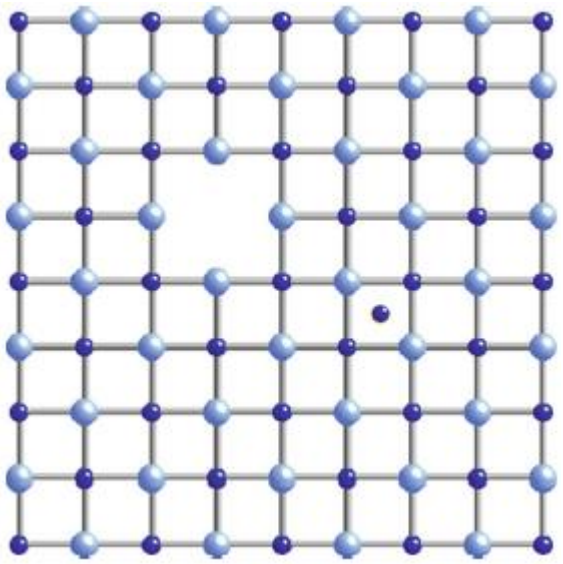
- If an atom is not present on the site that it should occupy in a perfect crystal, then a vacancy is located at that site.
- A Schottky defect is a set of vacancies created by removing one atom for each atom in the chemical formula.
- Thus, in a stoichiometric crystal such as MgO, we get a pair of vacancies, one on the Mg sub lattice and one on the O sub lattice.

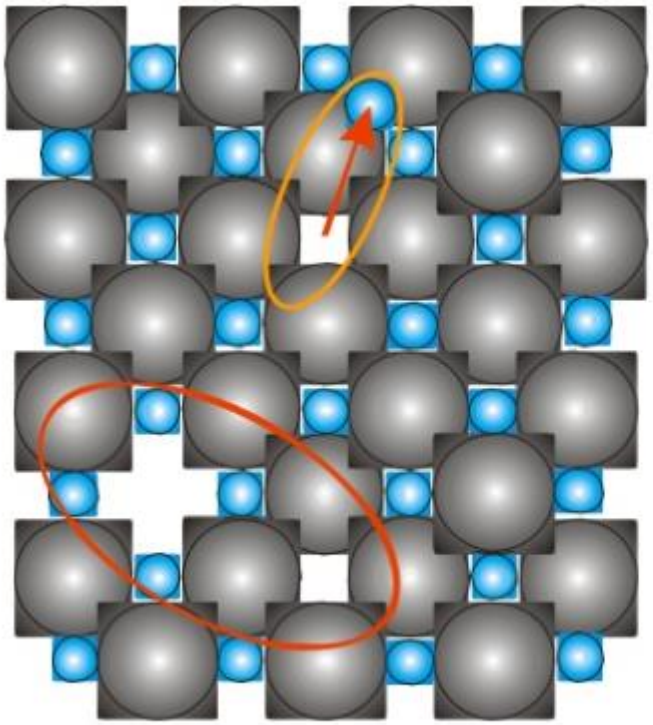


Types of point defect

Interstitials

- If an atom is present on any site that would be unoccupied in a perfect crystal, then that atom is an interstitial.
- A Frenkel defect is a vacancy + interstitial pair formed by removing an atom from its site in the crystal structure and putting it into an interstice
- Frenkel defects formed in iodine-containing AgBr are essential to the photographic process
- Occur due thermal vibration
- Occurrence depend on
  - size of ion
  - charge of ion
  - electronegativity
  - temperature





Frenkel defect

Cation vacancy
+
cation interstitial

Schottky defect

Cation vacancy
+
anion vacancy

Schottky defect	Frenkel defect
1. It is due to equal no. of cations and anions missing from lattice sites. 2. It results in decrease in density of crystal 3. This is found in the highly ionic compounds with having cations and anions of same sizes NaCl, CaCl	1. It is due to missing of ions [usually cations] from the lattice sites and these occupies interstitial sites. 2. It has no defect on the density of crystal. 3. This is found in crystal with low coordination no. Example:- AgI, ZnS etc.

Types of point defect

Misplaced atoms

- If an atom is present on a crystal site that should be occupied by a different atom, that atom is a misplaced atom and may be called an antisite defect.
- Antisite defects usually form in covalent ceramics such as AlN and SiC but can also occur in complex oxides that have several different types of cation (e.g., spinels, garnets).

Types of point defect

Associated centers

- When two point defects interact so they can be considered a single defect, they are called an associated center or, if more atoms are involved, a defect cluster or a defect complex.
- Exposing a material to ionizing radiation such as X-rays and g-rays can create large numbers of defect clusters.

Solute (substitutional) atoms

- In Cu alloys, we can add up to 30 at.% Zn before the structure is changed. All the Zn atoms sit on Cu sites, so they substitute for the Cu; and the crystal is said to be a solid solution of Zn in Cu.
- We can similarly substitute Ge in Si, but the solubility is limited due to the difference in atomic size.
- This type of substitution occurs in both covalent and ionic ceramics and also in metals.

Types of point defect

Impurities Defects

- Defects in ionic compounds due to replacement of ions by the ions of other compound is called impurities defects.
- For Example in NaCl, during crystallization; a little amount of $SrCl_2$ is also crystallized.
- In this process, Sr^{2+} ions get the place of Na+ ions and create impurities defects in the crystal of NaCl.
- In this defect, each of the Sr^{2+} ions replaces two Na+ ions. Sr^{2+} ion occupies one site of Na+ ion; leaving other site vacant.
- Hence it creates cationic vacancies equal number of Sr^{2+} ions.

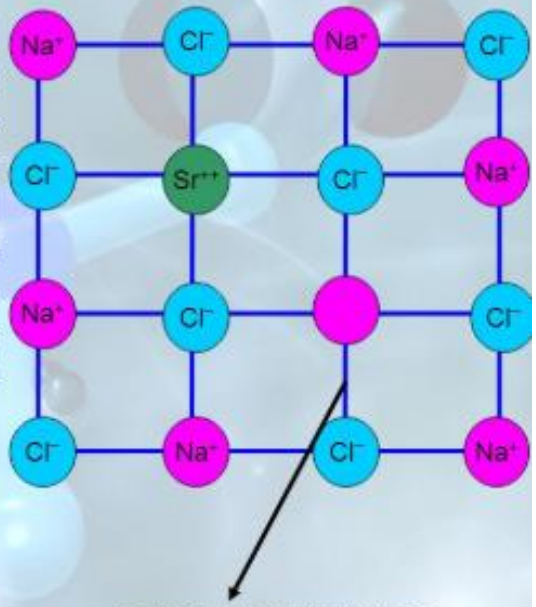
Electronic defects

- Electrons and holes can both exist in ceramics.
- They may be associated with particular ions, in which case they are simply charged point defects.

IMPURITY DEFECT IN IONIC SOLID

These defect in ionic crystal arise due to the presence of some impurity ions at the lattice sites (in place of host ions) or at the vacant interstitial sites. If molten NaCl containing a little amount of $SrCl_2$ is allowed to crystallise,some of the sites of Na^+ ions are occupied by Sr^{++} ions

If NaCl is doped with 10^{-3} mol % of $SrCl_2$, what is the concentration of cation vacancy ?

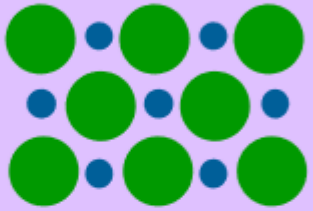


Impurities Defects

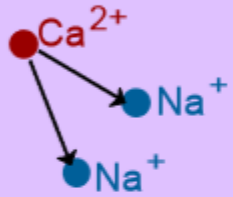
- Impurities must also satisfy charge balance = Electroneutrality

Example: NaCl 

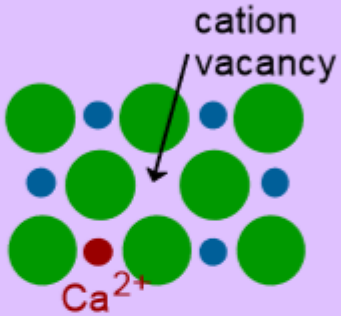
- Substitutional cation impurity



initial geometry

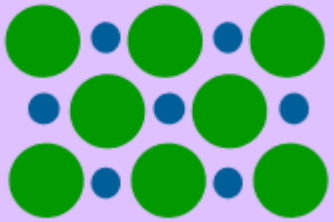


Ca^{2+} impurity

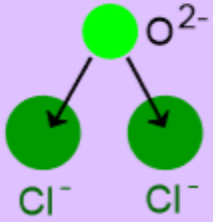


resulting geometry

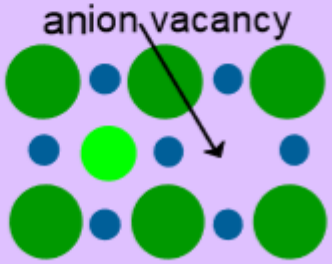
- Substitutional anion impurity



initial geometry



O^{2-} impurity



resulting geometry

What is special for ceramic

- Point defects are special in ceramics when they involve either charge (ionic materials) or dangling bonds (covalent materials).
- Vacancies, interstitials, and substitutional defects can all be charged.
- The special point defect in ceramics is the charged vacancy.
- Frenkel and Schottky defects are overall neutral.
- Association of defects is particularly important for ceramics because Coulombic interactions are both strong and long range.
- Electronic structure is increasingly important.
- In the past, the electronic structure was important only because the materials have a large band gap.

What is special for ceramic

- Ionic materials are insulators. This is no longer the case—many old "insulators" (e.g., SiC) are now also wideband- gap semiconductors!
- Nonstoichiometry is important because the concentration of point defects can be very large.
- In ionic materials, point defects are usually charged, and they are often numerous.

Some special rules for ceramics:

- The number of sites is constant.
- This is the same as in metals, but we often have very different sites available in ceramics.
- The total charge is still zero.
- Intrinsic defect concentrations are often very much lower than impurity concentrations.