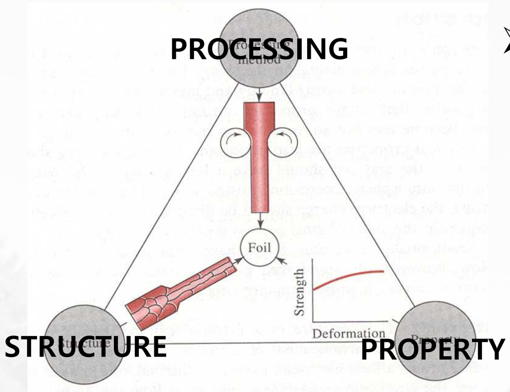
- **Crystal**
  - ✓ An anisotropic, homogeneous body consisting of a **3-dimensional periodic ordering** of atoms, ions, or molecules
  - ✓ In addition to their microscopic structure, large crystals are usually identifiable by their macroscopic geometrical shape, consisting of flat faces with specific, characteristic orientations
  - ✓ Solids which possess **long-range, 3-dimensional molecular order**

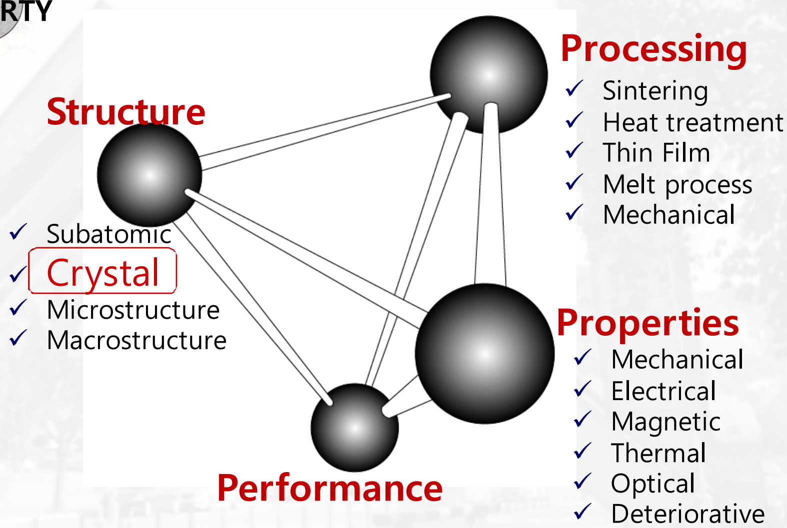
- **Crystallography** – concerned with the laws governing the **crystalline state** of solid materials with the arrangement of atoms (molecules, ions) in crystals and with their physical and chemical properties, their synthesis and their growth. (Ott)
  - ✓ 결정 구조와 이 구조에 기인하는 화학적, 물리적 성질을 연구하는 학문

- Perfect crystal vs. Crystals with defects

Materials Science & Engineering

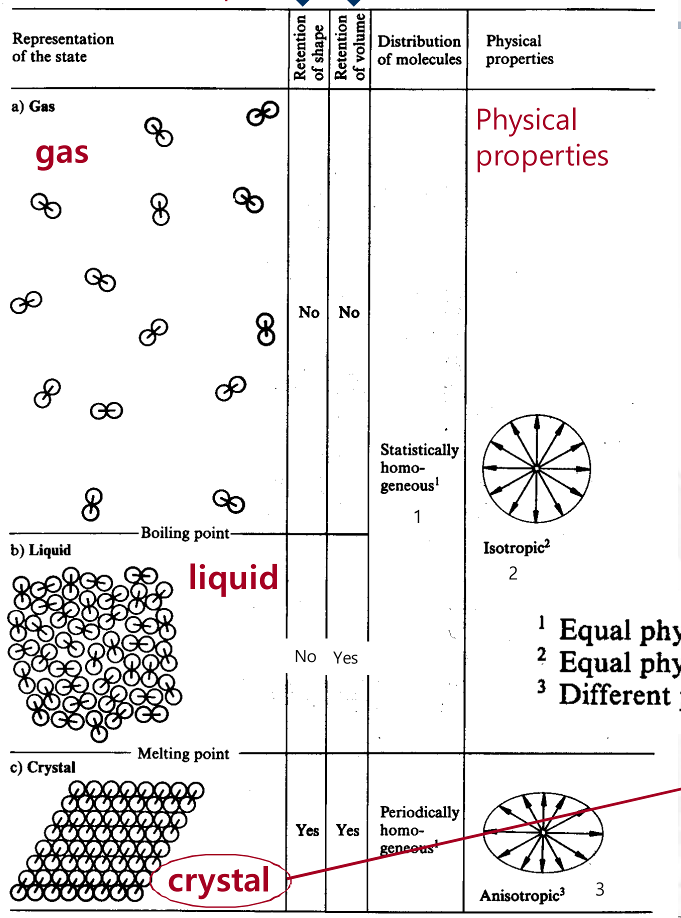


- Relation between
  STRUCTURE, PROPERTY & PROCESSING



Retention of shape | Retention of volume

Schematic representation of the states of matter

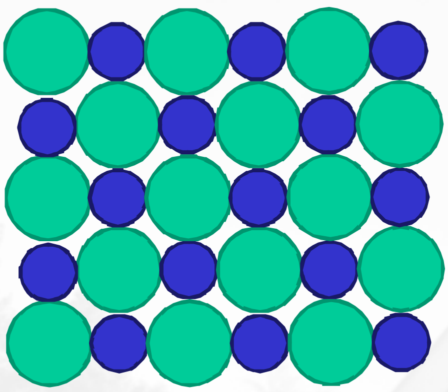


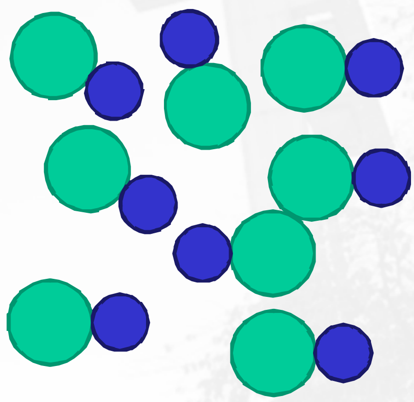
1 Equal physical properties in parallel directions
2 Equal physical properties in all directions
3 Different physical properties in different directions

Not "solid"

"Crystal" vs. "Solid"

Crystalline vs Amorphous (non-crystalline)





Crystalline

Short range order (O)

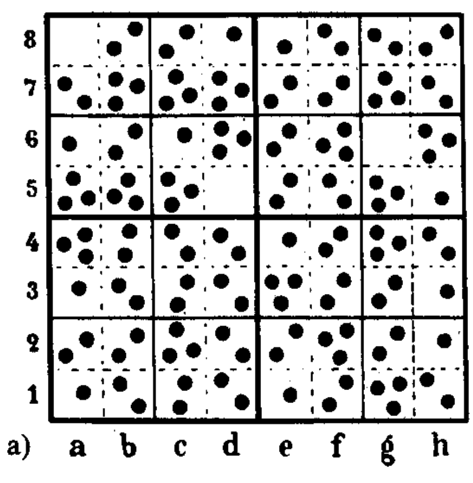
Long range order (O)

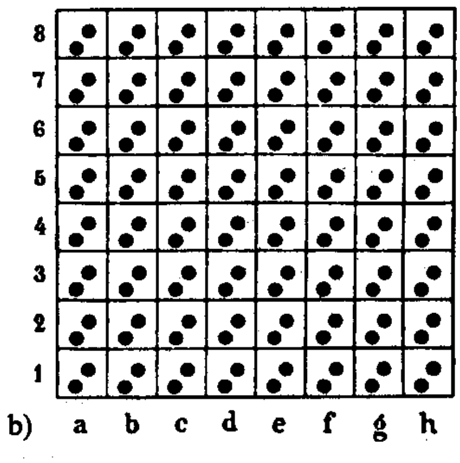
Amorphous

Short range order (X or O)

Long range order (X)

Homogeneity





Statistical homogeneity

: the same behavior in parallel directions → **isotropic** properties

Periodic homogeneity

: different behavior in different directions → **anisotropic** properties

Ott Chap 2

Anisotropy vs. Isotropy

- Anisotropy (이방성)
  - ✓ different values of a physical property in different directions
  - ✓ variation of a physical property with direction
  - ✓ tensor
- Isotropy (등방성)
  - ✓ same value of a physical property in all directions
- In general, most solids are anisotropic with respect to some physical parameters, but isotropic to others
  - ✓ ex) solid NaCl is optically isotropic but mechanically anisotropic
- What feature of the structure of the solid state give rise to anisotropy?

  → **internal structure** of crystals

Anisotropy in electrical properties

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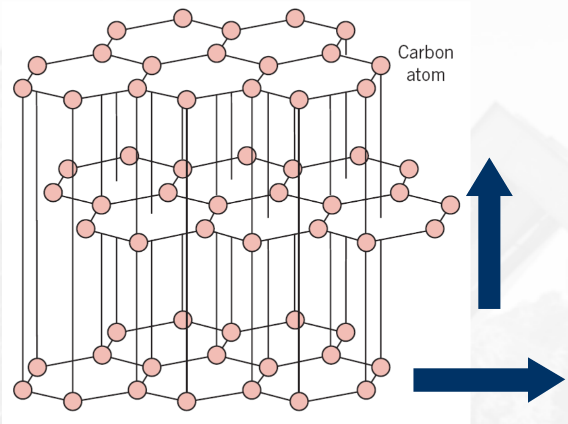
- Electrical conductivity
  - ✓ Graphite is anisotropic with respect to electrical conductivity



Graphite

Anisotropy in mechanical properties

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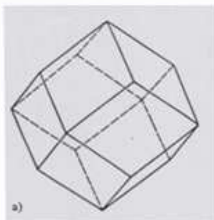
- Cleavage(벽개) - flat surfaces parallel to crystallographic planes
  - ✓ Fracture in glass - irregularly shaped pieces

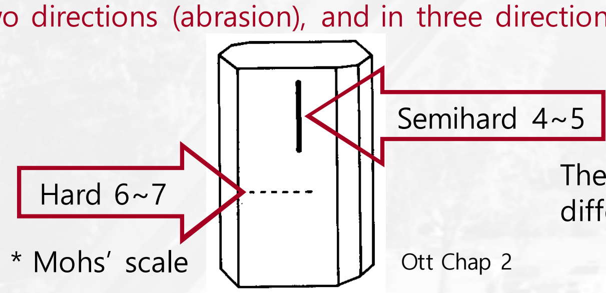
Rhombohedral cleavage of calcite ($CaCO_3$)



rhombo-dodecahedron

Ott page 2

- Different deformation in different directions
- Hardness (경도) - resistance to external stresses in one direction (scratching), in two directions (abrasion), and in three directions (penetration)



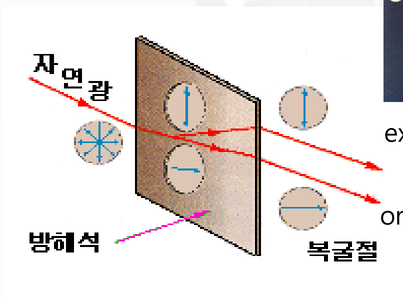
* Mohs' scale

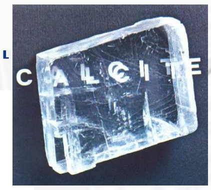
Ott Chap 2

The hardness of kyanite(Al_2OSiO_4) is different in the two directions

Anisotropy in optical properties

- Birefringence (복굴절) - formation of two polarized light waves traveling in different directions, i.e. production of two rays of polarized light
  - ✓ ex) calcite ($CaCO_3$)

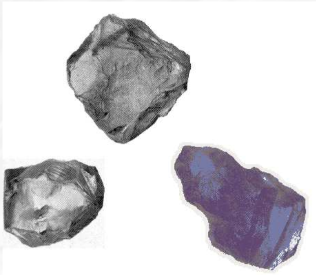


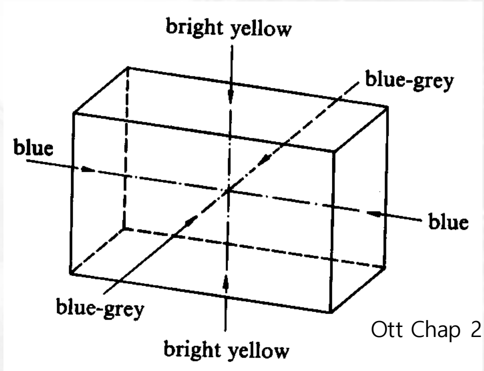


extraordinary ray

ordinary ray

- Pleochroism (다색성) - display more than one color due to the different absorption of light in different directions (dichroism, trichroism)

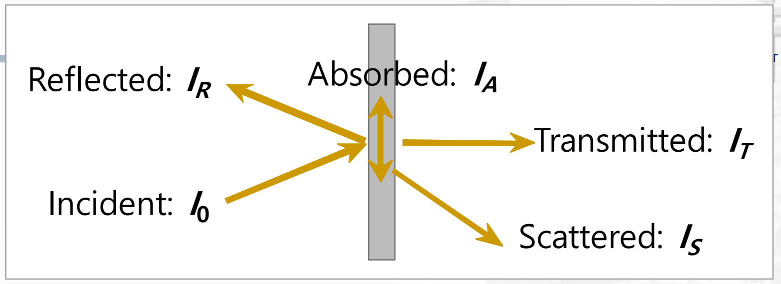




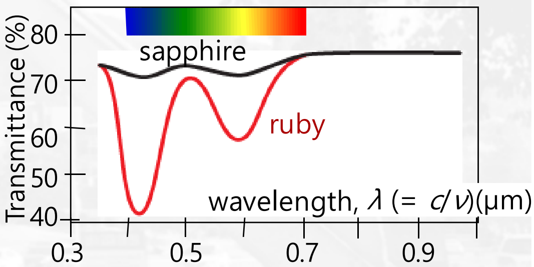
Ott Chap 2

cordierite ($Mg_2Al_4Si_5O_8$)
orthorhombic

Optical properties

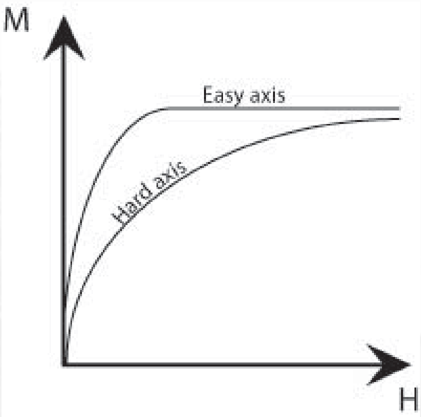


- Example 1: Cadmium Sulfide (CdS), E_g = 2.4 eV
  - -- absorbs higher energy visible light (blue, violet)
  - -- color results from red/orange/yellow light that is transmitted
- Example 2: Ruby = Sapphire (Al_2O_3) + (0.5 to 2) at% Cr_2O_3
  - -- Sapphire is transparent and colorless (E_g > 3.1 eV)
  - -- adding Cr_2O_3 :
    - alters the band gap
    - blue/orange/yellow/green light is absorbed
    - red light is transmitted
    - Result: Ruby is deep red in color

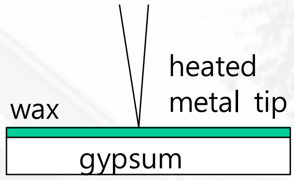


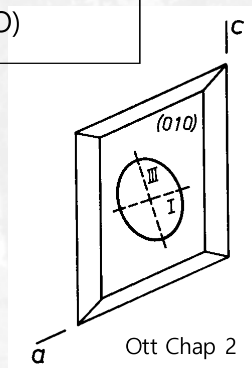
Anisotropy in magnetic & thermal properties

- Ferromagnetic materials can be magnetized more easily in some direction than in others → easy direction



- Thermal expansion coefficient
- Thermal conductivity
  - ✓Gypsum ($CaSO_4$ $2H_2O$)





Ott Chap 2

Thermal conductivity in direction III > that in direction I

→ ellipsoidal rather than circular

Coupled effects – Pyroelectricity & Piezoelectricity

- Pyroelectricity – appearance of electrical potential difference across the solid when the material is heated
- Piezoelectricity - appearance of electrical potential difference in response to mechanical pressure on the material
- Magnitude & direction of the potential difference varies according to the direction of heat flow or the pressure

Characteristics of solid state

- High density
- Fixed size & shape
- Resistance to shear stress

&

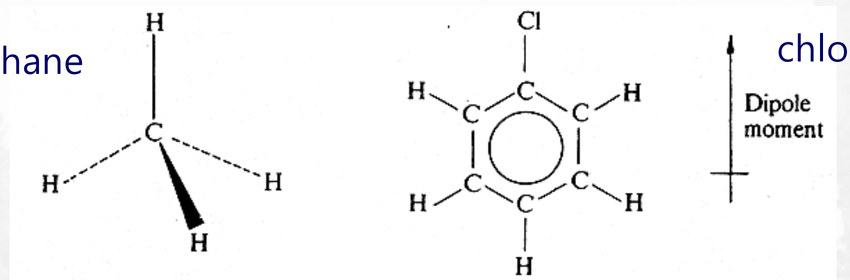
- Anisotropy (Crystal)

- All gases are isotropic in all their physical properties
- Most liquids are isotropic

Anisotropy, directional property

- What feature of the structure of the solid state will give rise to anisotropy?

methane



chlorobenzene

Molecular structure can give rise to anisotropy

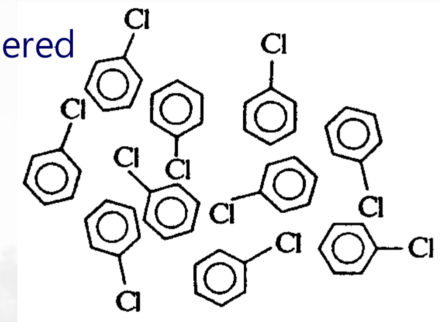
Variations in chemical structure can give rise to **directional properties**

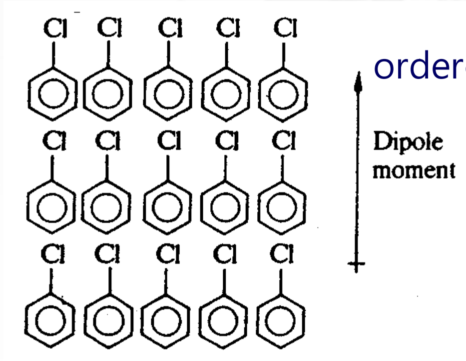
Sherwood Chap 1

Chlorobenzene molecules packed together in 2 different ways

Which of these structures is anisotropic?

disordered



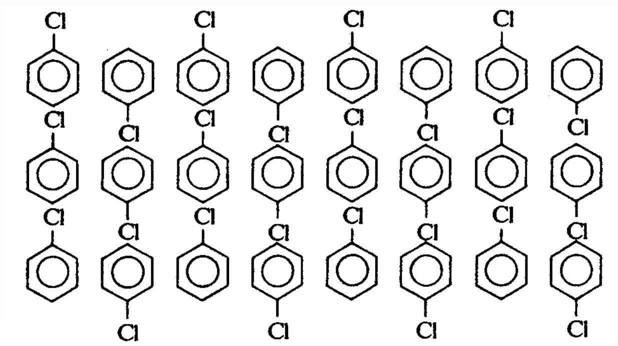


ordered

A random array	A regular array
No net dipole moment in any direction → isotropic dielectric constant	a net dipole moment → macroscopic anisotropy → anisotropic w.r.t. dielectric constant

- Definite, well-defined, ordered array → directional properties
- Anisotropy is only possible when the molecules are arranged with regularity and order

Array of chlorobenzene molecules which is ordered but which has no net dipole moment

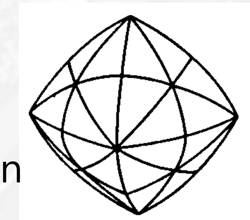


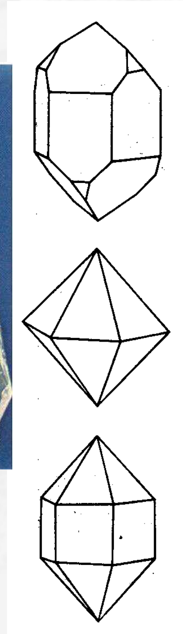
- Dipole moments cancel in pairs → dipole moment = zero in all directions
- Ordered, but no anisotropy.
- Isotropic with respect to its dielectric constant

- It is not correct to say that all ordered arrays will be anisotropic
- But it is undoubtedly true to say the converse, namely, that all anisotropic materials have an ordered structure

Diamond (C)

Quartz (SiO2)





Cubic, Octahedron

Hexagonal, Prismatic

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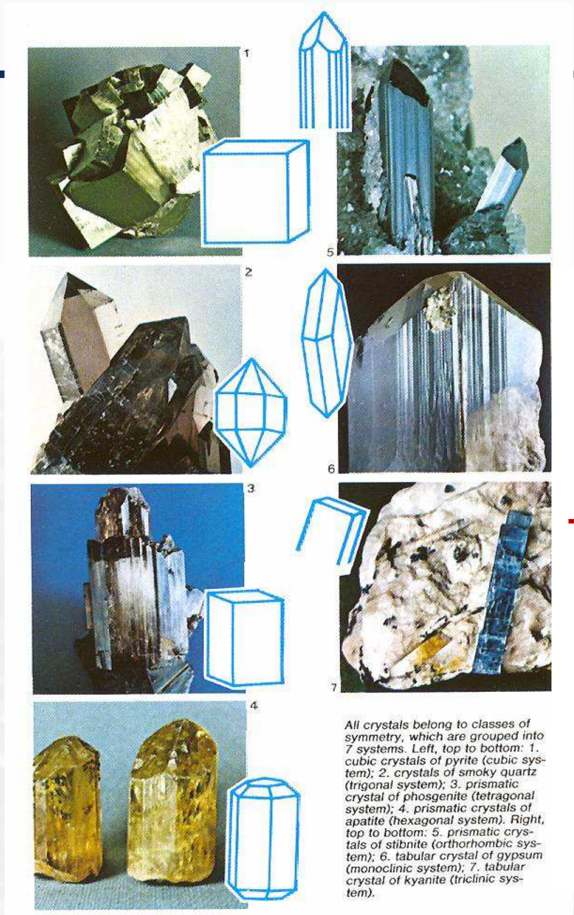
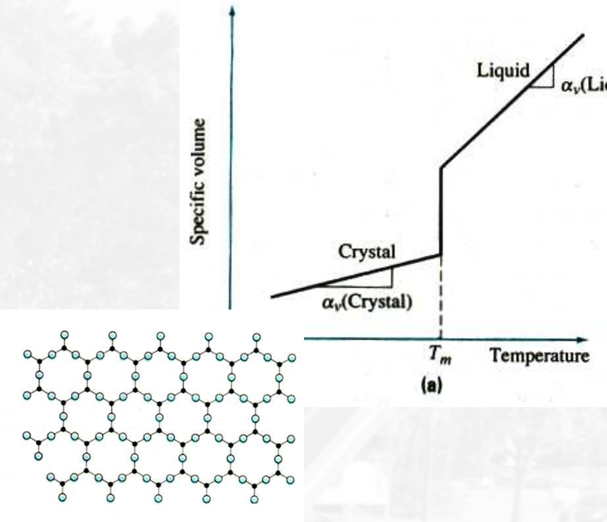


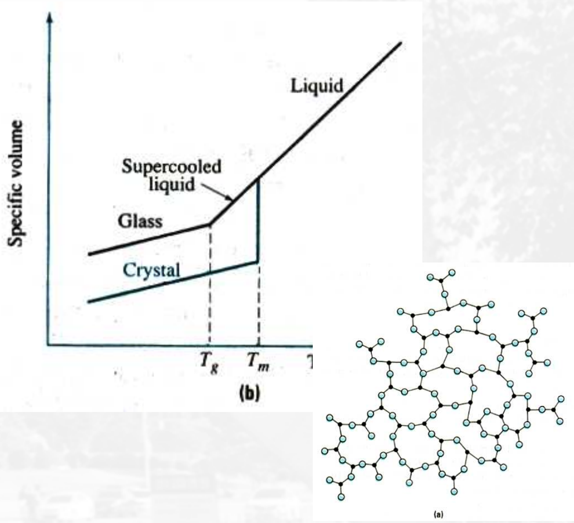
All crystals belong to classes of symmetry, which are grouped into 7 systems. Left, top to bottom: 1. cubic crystals of pyrite (cubic system); 2. crystals of smoky quartz (trigonal system); 3. prismatic crystal of phosgenite (tetragonal system); 4. prismatic crystals of apatite (hexagonal system). Right, top to bottom: 5. prismatic crystals of stibnite (orthorhombic system); 6. tabular crystal of gypsum (monoclinic system); 7. tabular crystal of kyanite (triclinic system).

Simon & Schuster's Guide to Gems and Precious Stones

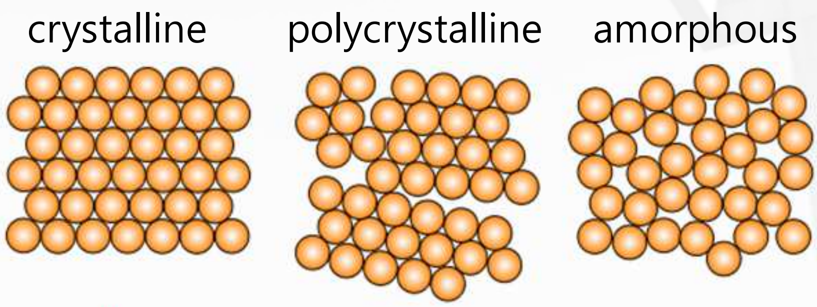
Are all solids crystalline? NO

- Crystal – <u>solids with long-range, three-dimensional molecular order</u>
  - ✓ Regular geometric shape
- <u>Solids which are not crystals – amorphous (non-crystalline)</u>
  - ✓ Glasses – do not have regular three-dimensional structure, do not have a sharp melting point → not crystalline





Crystalline, polycrystalline & amorphous

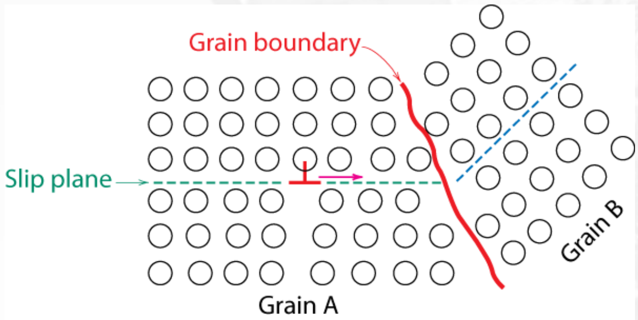


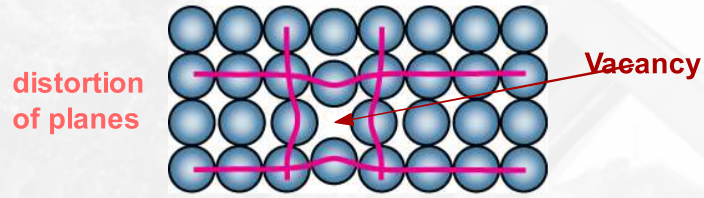
Microscopically,

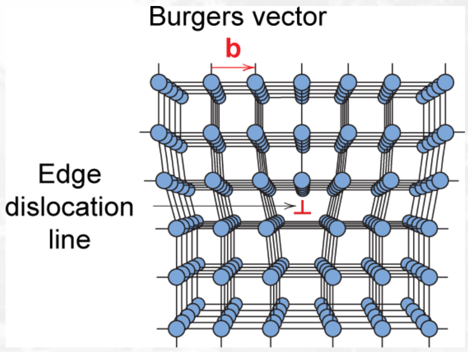
- a <u>single crystal</u> has atoms in a near-perfect periodic arrangement.
- a <u>polycrystal</u> is composed of many microscopic crystals (called "**crystallites**" or "**grains**").
- an <u>amorphous solid</u> (such as glass) has no periodic arrangement even microscopically.
- Example: <u>quartz</u> (crystalline SiO_2) vs <u>fused silica</u> (amorphous SiO_2)

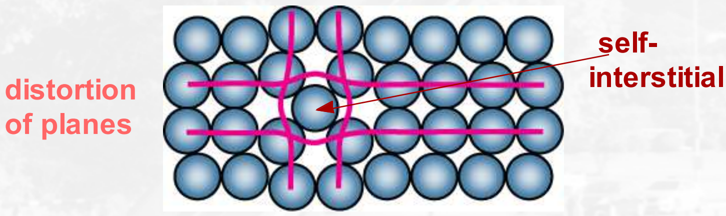
Perfect crystal vs. Crystals with **Defects**

Vacancy atoms	Point defects
Interstitial atoms	
Substitutional atoms	
Dislocations	Line defects
Grain Boundaries	Area defects
Surface	









todos

- Get the books
- Read before next class
  - ✓ Sherwood & Cooper Chapter 1 (1.7의 electron microscopy, AFM 부분 제외)
  - ✓ Ott Chapter 1, 2
  - ✓ Hammond Chapter 1.1, 1.2, 1.3
  - ✓ Krawitz 2.1, 2.2

Sherwood Chapter 1.9

- We do have means to focus X-ray.
- Focused X-ray as small as < 1um can be used.
- X-ray microscope exists. (the way they work can be different from that in optical/electron microscopy)