Chem 8201 – Materials Chemistry – Learning Objectives

Introduction to Crystal Structures

- Understand the concepts of unit cells, unit cell parameters, and fractional coordinates
- Know the 7 crystal systems and the 14 Bravais lattices
- Know how to count lattice points/atoms/molecules per unit cell (*Z*)
- Understand the concept of centering
- Be able to use density calculations to determine *Z* or unit cell size, defects, and porosity
- Know and understand the use of crystallographic point group elements and operations (both Schoenflies and Hermann-Mauguin notations)
    - Identity
    - Rotations (2, 3, 4, 6)
    - Inversion
    - Reflection
    - Rotation/inversion or rotoreflection
- Be able to assign point groups from symmetry elements using flowchart
- Know and understand the use of translational symmetry operations
    - Screw axes
    - Glide planes
- Understand the concept and naming of space groups
- Identify crystal systems and major symmetry elements from space group names
- Be able to identify symmetry elements from space group diagrams
- Understand the concept of Miller indices and assign Miller indices to lattice planes in unit cells
- Understand and apply the relationship between *d*-spacings, unit cell parameters, and Miller indices
- Understand the concepts of atom packing, atom coordination, polyhedral notation, and interstitial positions (octahedral, tetrahedral holes)

Structure Types

- Know the following ionic structures (packing of ions, types of interstitial sites filled, fraction of interstitial sites filled, coordination of ions)
    - Halite structure
    - Fluorite/antifluorite structure
    - Zinc blende/wurtzite structure
    - NiAs structure
    - CsCl structure
    - Inert pair effect
    - van der Waals layered structures
    - Corundum Structure
    - Rutile structure
    - Perovskites
    - Spinels
    - Olivines
- Visualize structures using physical models and computer models (e.g., CrystalMaker)

- Understand concepts of bonding in non-ionic structures
    - Atomic structures
    - Molecular structures
    - Covalent structures (including interpenetrating networks)

Carbon Materials
- Know the major allotropes of carbon, their structures, bonding interactions, and their most important physical properties
    - Diamond (including synthesis)
    - Graphite
    - Graphene
    - Graphene oxide (including synthesis of graphene and graphene oxide)
    - Carbon nanotubes (including synthesis)
    - Fullerenes
    - Disordered types of carbon
    - Porous carbon materials
- Understand how the structures relate to properties and applications
- Understand the concepts of intercalation and exfoliation
- Understand the application of Raman spectroscopy to characterize carbon materials

Silicates and Silica-based Materials
- Know the building blocks of silicates (0D, 1D, 2D, 3D)
- Be familiar with different polymorphs of crystalline silica
- Know the structures of silicate-based clays
- Understand the difference in intercalation of clays vs. graphite
- Be familiar with the compositions and properties of silicate-based glass and glass-ceramics

Porous Materials
- Know about primary, secondary, and tertiary building units of zeolites
- Know the structures of representative and important zeolites
    - Sodalite
    - Zeolite A (LTA)
    - Zeolite X (Y, FAU)
    - Zeolite Rho
    - ZSM-5 (Silicalite, MFI)
- Understand the structure/property/application relationships for zeolites
    - Host-guest materials
    - Size/shape-selective catalysts and sorbents
    - Ion exchangers (know how ion exchange can modify pore size)
    - Dessicants
- Know the process of hydrothermal synthesis applied to zeolites
- Understand the concepts of structure directing agents and templates
    - soft-templating with surfactant micelles
    - hard templating with colloidal particles and colloidal crystals
    - nanocasting

- Know the IUPAC definitions of microporous, mesoporous, macroporou, nanoporous
- Know about the differences in composition, structure, and bonding between the following coordination polymers
    - Hoffman clathrates
    - Metal–organic frameworks (MOFs)
    - Zeolitic imidazole frameworks (ZIFs)
    - Covalent organic frameworks (COFs)
    - Conjugated microporous polymers (CMPs)

Noncrystalline Materials

- Understand the differences in structural order and properties of the following classes of materials
    - Crystals
    - Plastic crystals
    - Quasicrystals
    - Liquid crystals
        - Lyotropic
        - Thermotropic (nematic, cholesteric, smectic)
    - Amorphous solids
- Know about appropriate characterization techniques for noncrystalline solids
- Understand structural phase transitions in these classes of materials

Powder X-ray Diffraction (XRD)

- Know the various application of powder XRD: what can be learned by this method?
- Understand the processes involved in the generation of X-rays
- Be familiar with the components of a powder X-ray diffractometer and their functions
- Know the features of a powder pattern (position, intensity, linewidth of peaks) and how a 1D pattern relates to a 2D pattern
- Derive and apply Bragg's law
- XRD patterns of crystalline vs. non-crystalline materials
- Know typical penetration depths and detection limits of XRD
- Understand the steps needed to identify composition of samples by powder XRD (manually and with automatic software)
- Become familiar with features of the ICDD data base
- Know how to index simple powder patterns and use them to determine unit cell parameters
- Be aware of potential pitfalls when indexing patterns
- Understand systematic absences and how these are used to determine lattice types
- Understand the differences between XRD patterns of physical mixtures and solid solutions
- Use Vegard's law to predict lattice parameters of solid solutions
- Understand the concept of superstructures and their effects on powder patterns
- Understand the factors contributing to peak intensities
    - Multiplicities
    - Structure factor
    - Form factor
    - Temperature factor

- Polarization factor
- Lorentz factor
- X-ray absorption
- Various instrumental factors
- Understand the concept of preferred orientation, its implication, and how to deal with it
- Understand the causes of line broadening and what can be learned from line broadening about the sample
  - grain size effects (Scherrer equation)
  - non-uniform stresses on particles
- Know the steps involved in Rietveld refinement procedures
- Be able to interpret XRD patterns from the literature

Neutron Diffraction (ND)

- Understand the differences in interactions between neutrons and matter vs. X-rays and matter
- Know which types of materials systems are most applicable for analysis by ND
- Know the information that can be obtained from ND for those systems and what is complementary to information obtained by XRD
- Understand the concept of time-of-flight analysis
- Understand the difference between chemical structure and magnetic structure

Electron Diffraction (ED) – Brief comparison to XRD & ND (more later in TEM lectures)

- Know which types of materials systems are most applicable for analysis by ED
- Know the advantages and disadvantages of using ED vs. XRD vs. ND
- Identify unit cell information from ED patterns for simple structures
  - Orientation
  - Crystallinity
  - Unit cell size
  - Crystal system from systematic absences

Electronic Properties of Materials

- Understand the concept of electrical conductivity and the factors contributing to it
  - Number of charge carriers
  - Charge
  - Mobility of charge carriers
- Understand simple and complex electronic band diagrams for solids
  - Metals
  - Semimetals
  - Semiconductors
  - Insulators
- Recognize examples of these different types of conductors and relative conductivities
- Understand the differences of temperature dependence of conductivity for these different types of conductors and the reasons for these differences (also including conducting polymers)
- Understand the concepts of Fermi energy levels, Fermi surfaces, and work functions
- Know the difference between intrinsic and extrinsic semiconductors

- Understand the concept of semiconductor doping and the effects of doping on electronic properties and band diagrams
- Understand the concepts of wave vectors, reciprocal space, and Brillouin zones
- Understand how Bloch orbitals and crystal orbitals relate to wavefunction
- Understand the derivation of 1D and 2D band diagrams in a qualitative way (relative energies of bonding and antibonding orbitals)
- Understand the concepts of bandwidth and band filling in band diagrams
- Understand the concept of density of states in 1D, 2D, and 3D materials
- Know the meaning of what is shown in a band diagram to be able to recognize the different classes of materials from the band diagram and understand relevant transitions
- Interpret band diagrams from the literature and from Materials Project
- Understand the difference between direct and indirect bandgap transition
- Understand how band structure relates to optical properties of materials
- Understand how bands can be tuned to modify optical properties
- Understand how metal–semiconductor rectifiers and MOSFETs work using band diagrams
- Understand electronic conductivity properties and mechanism of organic materials
    - charge transfer complexes
    - conducting polymers
- Understand the concepts of Peierls distortion, solitons, polarons, bipolarons
- Know the difference between doping of inorganic semiconductors and organic conductors

Nanoparticles and Quantum Size Effects
- Understand how confinement effects/quantum size effects/nanoparticle structure affect the following properties:
    - Density of states
    - Optical properties
    - Electronic properties
    - Phase changes
    - Reactivity

Materials Synthesis
- Understand the steps involved in high-temperature solid state synthesis (shake & bake synthesis, ceramic synthesis)
- Understand the concepts of topotactic and epitactic reactions
- Be aware of rapid heating methods
    - Spark plasma sintering
    - Ultrafast high temperature sintering
    - Microwave heating
- Understand the effects of atmospheres on controlling product composition
- Understand the advantages of precursor methods to improve product homogeneity
- Understand crystal growth processes and how morphology depends on relative growth rates of specific crystal faces
- Understand various crystal growth processes
    - Hydrothermal synthesis
    - Solvothermal synthesis

    - Ionothermal synthesis
    - Gel growth
    - Melt synthesis
        - Czochralski method
        - Kyropoulos method
        - Bridgman-Stockbarger method
        - Flame fusion method
        - Arc techniques
        - Skull melting
        - Zone refining
- Understand the concepts of congruent and incongruent melting
- Know how to prepare a silicon wafer starting from natural resources
- Understand the concept of materials synthesis/purification by chemical vapor-phase transport methods
- Understand various thin film growth processes
    - Physical deposition/coating
        - Dip coating
        - Spin coating
        - Cathode sputtering
        - Vacuum deposition
        - Pulsed laser deposition
    - Chemical deposition/growth
        - Liquid phase epitaxy
        - Molecular beam epitaxy
        - Chemical vapor deposition
        - Atomic layer deposition
        - Self-assembled monolayers
    - Electrochemical deposition
        - Cathodic deposition/electroplating/electrodeposition
        - Electroless deposition
        - Anodic oxidation
        - Thermal oxidation