Chem 5210 – Materials Characterization – Learning Objectives

Introduction to Materials Characterization and Important Background Concepts

- Understand the concepts of unit cells, unit cell parameters, and fractional coordinates
- Know the meaning of the 14 Bravais lattices
- Understand close-packing
- 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

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

Small-angle X-ray Scattering (SAXS)

- Know the various application of SAXS: what information can be gained from this method?
- Understand the scattering processes and the definition of scattering vector (similar to Bragg's law but in reciprocal space)
- Be familiar with the components of the SAXS instrument and their roles
- Understand the data workflow (2D → 1D, background correction)
- Know the information gained from the various regions in the scattering plot
    - Guinier plot, radius of gyration, particle shape
    - Fourier, cross-section structure & shape, pair-distance distribution functions
    - Porod, surface per volume
- Understand the roles of structure factor and form factor in the different models
    - Dilute particles
    - Concentrated particles
    - Periodic systems
- Understand the effects of contrast and contrast matching in multi-phase systems
- Know about the implications of volume effects on scattering intensity
- Learn how to interpret and apply SAXS data from the literature

Grazing-incidence Small-angle X-ray Scattering (GISAXS)

- Understand the difference between SAXS and GISAXS
- Know which types of materials systems are most applicable for analysis by GISAXS
- Know the information that can be obtained from GISAXS for those systems

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

Microscopy Concepts

- Know the differences in typical magnification, resolution, and general sample requirements for optical microscopy, SEM, TEM, and X-ray microscopy and their respective advantages/disadvantages
- Know the components their functions of the following types of optical microscope:
  - Conventional microscope
    - bright field
    - dark field
  - Inverted microscope
  - Phase contrast microscope
  - Differential interference contrast microscope
  - Polarized light microscope
  - Confocal microscope
- Understand sample preparation methods needed for the different types of optical microscopy
- Understand the following concepts used in microscopy
  - Magnification
  - Field of view
  - Depth of field
  - Numerical aperture
  - Resolution
- Understand the different types of lens aberrations and methods of correcting for these
  - Spherical aberration
  - Chromatic aberration
  - Astigmatism
- Understand the ways of achieving and enhancing contrast by the different optical microscopy methods listed above
- Understand the concepts relevant to digital microscopy
  - Nyquist sampling
  - Bit depth
  - Lossy vs. lossless file formats
  - Histograms and look-up tables
  - Grayscale vs. color
  - Image enhancement and ethical considerations
- Know how to analyze and critique optical microscopy images from the literature

Scanning Electron Microscopy (SEM)

- Know the various application of SEM: what information can be gained from this method?
- Know the critical limitations of SEM: resolution, magnification, sampling region
- Understand what the SEM can and cannot do
- Understand the different types of beam interactions with the sample
- Understand the structure of an SEM and the role of each component and how the component works
    - Electron gun
        - Thermionic emission
        - Field emission
        - Schottky emission
    - Vacuum system and water chilling system
    - Column
        - Electromagnetic lenses (condenser, objective)
        - Apertures
        - Deflection coils
    - Specimen chamber
    - Detectors
        - Secondary electrons
        - Backscattered electrons
        - X-ray detector (EDS)
        - Cathodoluminescence
    - Imaging system
- Understand sample preparation requirements and methods
- Understand how the different instrumental parameters affect the image quality (contrast, brightness, S/N, resolution, depth of field, depth of sampling, magnification)
    - Acceleration voltage
    - Aperture
    - Focus
    - Spot size (probe size)
    - Working distance
    - Scanning area
    - Scan rate
- Understand the different types of image artifacts and methods of correcting for these
    - Astigmatism
    - Edge effects
    - Charging
    - Specimen damage
    - Beam-related contamination
- Be aware of specialized SEM techniques and their applications
    - Environmental SEM
    - Cryo SEM
    - Electron backscatter diffraction (EBSD)
    - Electron channeling contrast imaging (ECCI)
    - Electron beam lithography (EBL) and focused ion beam (FIB) lithography
- Know how to analyze and critique SEM images from the literature

Energy-Dispersive Spectroscopy (EDS)

- Understand the purpose and general applications of EDS
- Understand the mechanistic processes involved in EDS
    - Continuum X-rays vs. characteristic X-rays
    - Siegbahn notation
    - The EDS spectrum
- Understand the critical components of an EDS system and each of their functions
    - X-ray generation (discussed earlier in course)
    - EDS detectors and detection processes
    - Pulse processor
    - Multi-channel analyzer
- Understand what can be learned from qualitative EDS and what are the limitations
    - Interpretation of EDS spectra
    - X-ray peak identification
    - X-ray intensity
    - Spectral resolution
    - Spectral artifacts
    - Peak identification and peak misidentification
- Understand the steps in obtaining reliable quantitative EDS data
    - Optimal instrument parameters
    - Sample preparation
    - Spectral processing
    - Concentration calculations
    - ZAF corrections
    - Accuracy, precision, and detection limits
    - Errors in EDS analysis
- Understand the concepts involved in X-ray Mapping
    - Elemental maps
    - Parameters for X-ray mapping
    - Artifacts in elemental maps

X-ray Photoelectron Spectroscopy (XPS)

- Understand that XPS is a surface analysis technique and know the limitations of XPS (depth of analysis, spatial resolution)
- Understand what information can be obtained from XPS
  - Elemental identity
  - Chemical state
  - Quantity of elements
  - Spatial distribution when scanning (mapping)
  - Depth distribution when ion milling or using angle-resolved XPS
- Understand the critical components of an XPS system and each of their functions
- Understand the processes involved in photoelectron generation and the associated energies
  - binding energy
  - kinetic energy
  - photon energy
  - work function
- Know the typical workflow of XPS analysis
- Understand XPS spectra
  - Survey scans
  - High resolution scans
- Know what is involved in quantitative XPS analysis
- Understand final state effects and recognize the corresponding spectral features
  - Shake-up satellite peaks
  - Spin–orbit coupling
  - Auger electrons
  - Multiplet splitting
- Be aware of complications in XPS
- Know the information obtainable from angle-resolved XPS
- Know how to interpret XPS data from the literature
- Know the differences in limitations of XPS vs. EDS

Transmission Electron Microscopy (TEM)

- Understand what TEM can and cannot do
- Understand the electron beam interactions with the specimen
- Understand the components of a TEM and their functions
    - Electron gun
    - Electron column
    - Electromagnetic lens system with aperatures
    - Specimen chamber
    - Image capturing system
    - Detectors
    - Vacuum system (see section on SEM)
- Understand the image formation mechanism at various points in the column
    - Back focal plane (diffraction)
    - Image plane (imaging)
    - Bright-field images
    - Dark-field images
    - Phase-contrast imaging
- Understand the different mechanisms of obtaining contrast
    - Phase contrast
    - Amplitude contrast
    - Mass contrast
    - Diffraction contrast
- Understand the process of obtaining electron diffraction patterns, including selected-area electron diffraction (SAED) and convergent beam electron diffraction (CBED)
- Be able to interpret electron diffraction patterns (see earlier section on diffraction methods)
- Know the processes involved in instrument alignment to obtain better images
    - Condenser lens centering
    - Condenser lens stigmation
    - Eucentric position
    - Focus
    - Objective apertures
    - Objective lens astigmatism correction
- Understand how different parameters affect the image
    - Voltage
    - Condensor aperture size
    - Objective aperture size
    - Spot size
- Understand the operation and applications of scanning transmission electron microscopy (STEM)
- Understand the operation and applications of high-angle-annular dark-field (HAADF) STEM
- Be familiar with specimen preparation methods and requirements
- Be aware of specialized TEM methods
    - Liquid cell TEM
- Be aware of image artifacts and how to deal with them
    - Artifact introduced during sample preparation
    - Beam damage

- Spherical aberration, chromatic aberration, astigmatism (Aberration-Corrected TEM)

- Understand the application of EDS in TEM and know the differences compared to EDS in SEM
- Understand the purpose, general applications, and operating principles of electron energy loss spectroscopy (EELS)
- Understand the purpose, general applications, and operating principles of cryo-TEM and cryo-electron tomography
- Understand the purpose and general applications of electron crystallography

Atomic Force Microscopy (AFM)

- Know about the types of imaging possible using AFM
- Understand the general operation of an AFM
- Understand the forces of interaction between tip and sample in contact mode, tapping mode, and non-contact mode AFM
- Know the differences in operation and relative advantages/disadvantages for contact mode, tapping mode, and non-contact mode AFM
- Be aware of the different applications of these AFM modes
- Be aware of possible artifacts arising in the image and from the tip or scanner
- Be aware of related scanning probe methods
    - Scanning tunneling microscopy (STM)
    - Near-field scanning optical microscopy (NSOM)
    - Tip-enhanced Raman spectroscopy (TERS)
    - Photothermal-acoustic AFM-IR

Thermal Analysis

- Understand the applications of thermal analysis
- Understand the operation of a thermogravimetric analyzer (TGA)
- Interpret TGA and derivative thermogravimetry (DTG) curves both qualitatively and quantitatively
- Understand the parameters that affect TGA curves
- Use TGA data to determine sample composition
- Understand how differential thermal analysis (DTA) works
- Interpret DTA data
- Differentiate between exothermic and endothermic physical and chemical processes
- Understand how differential scanning calorimetry (DSC) works
- Interpret DSC data
- Know about hyphenated TGA methods (TGA-IR, TGA-MS, TGA-GC/MS)

Gas Sorption Analysis (focus on physisorption)

- Know about the types of porous materials that can be analyzed by gas sorption analysis and definitions of pore size ranges
    - micropores
    - mesopores
    - macropores
    - nanopores
- Understand what information can be obtained from gas physisorption analysis
    - specific surface area
    - specific pore volume
    - average pore size
    - pore size distribution
- Know definitions of terms related to sorption
    - Adsorption
    - Absorption
    - Physisorption
    - Chemisorption
- Know about the equipment and the process used for gas sorption analysis
- Understand the steps in the sorption process and relate them to the sorption isotherm
- Know about sample preparation requirements and choice of sample cells
- Know about the classification of isotherm and correlate isotherm shapes to different types of pore structure
- Understand hysteresis loops and how they relate to pore features
- Know about various types of adsorption models
    - Langmuir
    - BET
    - NLDFT
    - QSDFT
    - Monte-Carlo simulations
- Understand limitations of the BET model for calculating surface areas
- Understand limitations in determining pore size distributions
- Know how to interpret gas sorption data from the literature