MASTER
SOLID-STATE &
CRYSTALLIZATION
UNIVERSITE de ROUEN-NORMANDIE

UE 1-S3 : Solid-state : preparation and characterization

Prerequisite :

Basic knowledge in RMN and IR (Master 1 level)

Content of courses

- ***Solid-State NMR (Dr. C. Kouvatas) 15hCM***

Basic principles of RMN
Description of main differences between liquid and solid RMN
Which information can be deduced from structure of crystallized or amorphous materials
Which information could be obtained on physical and chemical properties?
Application to catalytic materials

Objectives : Bases on RMN for physical and chemical properties of solids. Specification for catalytic materials, in a academic or industrial framework.

- **Characterization of solids by vibrationnal spectroscopy (M. Daturi) 15h CM**

Introduction to IR and RMAN spectroscopy, principles of instruments, signal treatment, in situ analyses and use of probe molecules, acid, basic redox properties of surfaces, and characterization of materials dedicated to catalysis. Application to physico-chemical properties of divided solid for catalysis.

Objectives :Formation to advanced vibrational spectroscopies, critical approach.

Evaluation :

Written exam

UE2-S3 Master 2 S2C – « Solid-state : Symmetry »

Prerequisite :

Knowledge of basics in crystallography

Content of courses

- **Crystalline and molecular Symmetry**

Reminder of the basics of Space groups and crystallography.

Crystals quasicrystals, mesophases, and amorphous (continuum). Reminder on the concept of group and theorem of isomorphism. 32 point groups, 4 modes, 73 synmorphic space groups and 230 space groups. Basic notion of color groups. 65 chiral groups, centrosymmetric groups and non-chiral & non-centrosymmetric groups. Superimposition of crystallographic and molecular symmetries. Pseudo-symmetries hyper-symmetries. Dimension of space necessary for description of incommensurable phases. Disordered molecular structures.

- **Electronic Microscopy**

This course aim at presenting the potentialities of electronic microscopy and associated techniques in material science and more particularly to crystallized nanomaterials.

By numerous examples, student will have a rationalized approach of this characterization technique.

Evaluation :

Written exam for each part

UE3-S3 Master 2 S2C « Crystallization processes »

Prerequisite :

Fundamentals of Crystallization (nucelation growth)
Knowledge about crystallization and growth theory
Characterization methods of solid state : XRPD, DSC, FTIR, microscopy)
Basics on crystallography.

Content of courses

- ***Nucleation/growth/defective crystals***

Advanced theory of nucleation and growth, implication in industrial processes.
Description of different types of defect (0D, 1D, 2D and 3D) present during crystallization processes.
A specific focus will be made on fluid inclusion formation mechanisms.
Prediction of crystal morphology

- **Industrial Crystallization**
- Description of industrial processes of crystallization
- Chemical engineering applied to crystallization
- Industrial property: Patent, Patentability (usefulness, inventiveness &-novelty- and enablement), different anticipations, Discovery of the PCT system, USPTO and EPO organizations, freedom to operate, patent litigation, pitfalls and benefits of patenting. Drafting a patent.

- **Bibliographic project** conducted on a crystallization process (oral presentation)

Evaluation :

Oral examination (bibliographic project)

Written exam for each part

UE4-S3 Master 2 S2C – « Molecular crystals »

Prerequisite :

Phase diagrams: unary, binary and basics of ternary systems.
Solid-state characterization (DSC, XRD, microscopy)
Extended knowledge in crystallography up to space groups and sub space groups. Single crystal X-ray diffraction.
Basic notion on XRay diffractogram exploitation : (determination of lattice parameter and space group)
Basic knowledge in optic (1st cycle)

Content of courses

- **Specificity of molecular solids**

Thermodynamic of organic solids with their specific behaviour due to their chemical nature (hydrogen bonds, large possibility to cocrystallize, ability to polymorphism, interaction with solvent of crystallization).
By a permanent round trip between theory and examples coming from research experiences, students will be able to understand concretely the utility of phase diagrams for the rationalization of crystallization processes of organic solids and for their evolution during ageing or storage. Polymorphism, salts, solvates, cocrystals, host-guest associations ad hybrids. Dynamic and static disorder. Entropy of fusion. Chiral discrimination in the solid state. Desolvation mechanisms. Order – disorder transitions. Destructive – reconstructive transitions. Displacive transitions. Solid solutions and their consequences on purification by crystallization. Preferential crystallization and preferential enrichment

- **Characterization of molecular crystals**

Second harmonic generation spectroscopy. Principle of nonlinear optics, application to solid state characterization (phase diagram, polymorphic transitions, crystallinity, …)
Granulometry. Impact of particle size on the fabrication process, particle size distribution, experimental methods, application)
Nucleation
Crystal structure resolution of crystalline solids from X-ray diffraction data on polycrystalline or single crystalline samples together with the analysis of the obtained crystal structures. After a recall on the theory of X-ray diffraction by a crystal lattice, the methods used to solve crystal structures from single crystal and powder X-ray diffraction data will be described in detail. The methods of analysis of those crystal structures in terms of molecular packing and intermolecular interactions will be described as well.

- **Research project :**

Work group on a specific subject extracted from research context. Presence in the laboratory to have access to experimental apparatus.

Evaluation :

Oral and written examination

UE 5-S3 : Characterization of amorphous and crystalline solids

Prerequisite :

Connaissance des polymères, notions de physique de base

Connaissances de base de cristallographie (réseau cristallin, réseau de Bravais, plans réticulaires, loi de Bragg…)
Connaître la nomenclature des symétries cristallines (groupes ponctuels et groupes d'espace)
bases sur les états de la matière (solide/liquide/gaz), différences solide cristallin/amorphe et propriétés générales des solides moléculaires cristallisés (solubilités, point de fusion).

Content of courses

- ***Caractérisation des polymères à l'état solide (15 CM)***

Propriétés thermiques (8h CM): Analyse des polymères amorphes et semi-cristallins par diffraction des rayons X. Caractérisation des propriétés mécaniques d'un matériau polymère (traction, compression, cisaillement. Notions de viscoélasticité, viscoplasticité, hyper-élasticité, fatigue, indentation, fluage, relaxation. Microstructure d'un polymère à partir des mesures analyses thermiques. Exercices applicatifs, étude de cas.
Analyse thermique (7h CM) : Analyse Calorimétrique différentielle: principe, protocoles expérimentaux, exemples. Analyse Calorimétrique différentielle à Modulation de Température (MT-DSC): principe, protocoles, exemples. Vieillissement physique dans les polymères à l'état solide: définition, techniques calorimétriques associées pour le caractériser: DSC, MT-DSC, DSC ultra rapide

- ***Caractérisation des solides organiques cristallisés (15 CM)***

Résolution de structure cristalline par diffraction de Rayons X (8h CM) : Rappels sur la théorie de la diffraction des rayons X par un réseau cristallin puis présentation et description (théorie, appareillage, paramètres mesurés) de méthodes à base de rayons X pour l'analyse de matériaux amorphes ou polycristallins (diffraction des rayons X sur poudre –paramètres de maille, tailles de cristallites, taux de cristallinité-, small angle X-ray scattering –SAXS-, analyse de pair distribution function –PDF-, réflectivité X, …)
Analyse thermique sur matériaux cristallisés (7hCM) : brefs rappels sur l'analyse thermique (ATD/DSC); applications de la DSC aux solides organiques (polymorphisme, stabilité relative et règles thermodynamiques); implications du polymorphisme sur des binaires simples soluté/solvant; bénéfices des analyses couplées dans la caractérisation des composés définis (solvates/hydrates en particulier) et applications aux diagrammes binaires avec présence de composés définis.

Evaluation :

Written exam on each part

UE 5.2 : Chirality at the solid state

Prerequisite :

General formation in chemistry (master 1)

Content of courses

Generalities about chirality at the solid state (molecular chirality, supramolecular chirality, atropoisomerism)
Enatiomeric resolution processes by crystallization : Pasteurian resolution, preferential crystallization, deracemization)
Application of the aformentioned notions to an industrial context (e.g. continuous crystallization).

Evaluation :

Written examination

Semester 4

UE 1-S4 : Professional environment

English 20h
Preparation for the job interview 10h

Examination

Oral and written examinations

UE 2-S4 : Training period

5 to 6 months in an industry or research lab involved in the crystallization/solid-state domain (from February to June (or July)

Examination : (around mid july)

Scientific report

Oral Defense

Mark for investment