UNIVERSITÀ
DEGLI STUDI DI MILANO-BICOCCA

# SYLLABUS DEL CORSO

## Chimica dei Materiali Ceramici

**2627-3-ESM01Q014**

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### Aims

**1. Knowledge and Understanding**
• At the end of the course, the following will be acquired:
• Knowledge of the fundamental concepts of chemistry of ceramic materials, including crystal structures and the nature of chemical bonding
• Familiarity with the chemical-physical properties of ceramic materials (oxides, sulfides, carbides, etc.) and their applications
• Understanding of crystal field theory and the electronic structure of transition metal oxides
**2. Applying Knowledge and Understanding**
The following abilities will be acquired:
• Determine the basic properties of ceramic materials based on their composition and structure
• Identify the electronic properties of ceramic materials, particularly for transition metal oxides
• Relate the properties of ceramic materials to the chemical bonding between the elements that compose them
**3. Making Judgments**
• At the end of the course, students will be able to:
• Correctly interpret the chemical behavior of ceramic materials and relate it to structural, electronic, and magnetic properties
**4. Communication Skills**
Students will know:
• To express clearly and precisely the concepts covered in the course, using scientific language correctly
• To present and argue the course topics in a clear, organized, and rigorous manner
**5. Learning Skills**
During the course, the following will be provided:
• Methodological competencies to approach the study of master's degree courses
• The ability to consult specialized texts to independently deepen the concepts presented during lectures
• The ability to connect the topics covered in class

## Contents

The course describes the class of ceramic materials (oxides, sulfides, carbides). We recall basic notions of crystal structure and give information about the synthesis of materials in form of single crystals, polycrystalline phases, amorphous structures, thin film, fibers, microporous materials. We describe techniques of direct solid state synthesis, synthesis in solution (sol-gel, precipitation, hydrothermal synthesis), preparations from gas-phase precursors (chemical vapor deposition, etc.).

The second part deals with the properties of ceramic materials: thermal properties, mechanical properties, electrical behavior, magnetic and optical properties. Various classes of inorganic materials of particular applicative importance are then presented: low-dimensional systems (intercalation phenomena), zeolites and porous materials, oxides and sulfides for catalytic applications, glasses, cements, biocompatible inorganic materials.

The third part is dealing with the properties of transition metal oxides. After an analysis of the ionic bonding, Born-Haber cycle, etc., the course introduces the crystal field theory. Then advanced theories of bonding in transition metal oxides are described (Mott-Hubbard model, magnetic insulators, metallic oxides, etc.). The nature of the band gap in transition metal oxides is analyzed with the help of spectroscopic data. Defects and non-stoichiometric materials are also described.

## Detailed program

**PART ONE**
**1. Crystal Structures of Inorganic Solids**
Crystal structures of inorganic solids (NaCl, zinc blende (ZnS), fluorite (CaF?), and antifluorite (Na?O) structures - Diamond structure - Wurtzite (ZnS) and nickel arsenide (NiAs) structure - Cesium chloride (CsCl) structure - Other AX structures - Rutile (TiO?), cadmium iodide (CdI?), and cadmium chloride (CdCl?) structures - Perovskite structures (SrTiO?) - ReO? and tungsten bronze structures - Spinels structure - Silicates structure)
Relationship between ionic radii and crystal structures

**2. Synthesis of Inorganic Solid-State Materials**
Single crystal synthesis (Bridgman method - Stretching method - Verneuil method - Floating zone method - Crystallization from aqueous solution - Hydrothermal synthesis)
Polycrystalline and powder material synthesis (Solid-state reactions - Direct combination reactions - Solid solutions - Solid-gas and solid-liquid reactions - Evaporation reactions - Oxidation reactions - Thermal decomposition reactions - Chemical vapor deposition - Chemical vapor transport - Liquid phase reactions - Sol-gel method - Precipitation - Template precipitation (zeolite synthesis) - Spray-drying method - Freeze-drying method)
Thin film synthesis (Gaseous phase methods - Chemical vapor deposition, CVD - Substrate reaction method - Spray pyrolysis method - Vacuum evaporation method - Spray deposition method - Ion implantation - Liquid phase methods - Sol-gel method - Liquid phase epitaxy - Molten salt epitaxy - Solid phase methods)
Fiber synthesis (Glass fibers - Optical fibers)
Production of glassy materials

**3. Chemical-Physical Properties of Ceramic Materials**
Thermal properties (Melting point - Thermal conductivity - Thermal expansion)
Electrical properties (Electrical insulators - Ferroelectricity - Pyroelectricity - Piezoelectricity - Ceramic superconductors)
Magnetic properties (Ferromagnetic compounds: CrO? - Antiferromagnetic compounds: transition metal oxides - Ferrimagnetic compounds: ferrites (spinels))
Optical properties (Optical fibers - Optical switches - Materials for non-linear optics - Luminescence and phosphors - The laser)
Mechanical properties (Deformation and fracture - Hardness - High-temperature resistance (refractories))

**4. Low-Dimensional Solids**
One-dimensional solids (Platinum chain compounds)
Two-dimensional solids: intercalation compounds (Intercalation mechanism - Synthesis of intercalation compounds - Metal dithiogenate intercalates - Metal oxihalogen intercalates - Metal oxide intercalates - Graphite intercalates - Layered silicates and clays)
Inorganic nanotubes of layered materials

**5. Zeolites**
Structure and composition
Structure from NMR measurements
Zeolite use (Dehydrating agents - Zeolites as ion exchangers - Zeolites as adsorbents - Zeolites as catalysts)

**6. Catalysis Materials**
The catalytic cycle
Activity and selectivity
Active sites
Examples of heterogeneous catalysis (Hydrogenation catalysis - Ammonia synthesis - Asymmetric catalysis - Acid-base catalysis - Oxidation catalysis)
Catalysis materials (Oxides - Sulfides - Supported metals)

**7. Glasses**
Glass production and processing (Container glass production - Glass sheets - Glass tubes - Glass fibers)
Structure of glasses and silicates
Chemical and physical properties of glasses
Mechanical properties

**8. Cements**
Aerial and hydraulic binders
Historical notes
Portland cements and main constituent phases (Nomenclature in cement chemistry and abbreviations - Preparation method - Clinker formation - Alite: polymorphism - Belite: polymorphism - Aluminate phase)
Clinker phase hydration (Hydration: calorimetry - Proposed structures of calcium silicate hydrate)
Physical and mechanical properties (Special Portland cements)
Aluminous cements
Water stability of hydrates (Portland cements - Aluminous cement)
Cement additives
Solid-state magnetic resonance applied to cements (Low resolution - High resolution - NMR of silicates and cements)

**9. Biocompatible Ceramics**
Biogenic inorganic materials
Classification of biocompatible ceramics
Mechanical properties and biocompatibility
Biological materials
Bioceramics: classification by composition
Bioceramics: classification by application

**PART TWO**
**1. Bonding in Inorganic Solids**
Ionic bonding (Lattice energy of ionic crystals - Born-Haber cycle - Do pure ionic compounds really exist?)
Covalent character in ionic solids (Polar covalent bonding in solids)
Crystal field theory (Crystal field stabilization energy - Crystal field in tetrahedral symmetry - Electron coupling energy, P - Factors affecting 10Dq separation - Consequences of crystal field stabilization - Crystal field stabilization and spinel structure - Tetragonal distortion and Jahn-Teller effect - Square planar coordination - Crystal fields in other symmetries - The nephelauxetic effect)

Molecular orbital theory
Charge transfer spectra

**2. Solid-State Spectroscopies**
Vibrational spectroscopies: IR and Raman
Visible and ultraviolet spectroscopy
Nuclear magnetic resonance
Electron spin resonance
X-ray spectroscopies: XRF, AEFS, EXAFS (Emission techniques - Absorption techniques - AEFS EXAFS)
Electronic spectroscopies: ESCA, XPS, UPS, AES, EELS

**3. Transition Metal Oxides**
Band model
Hubbard model (Hubbard U and lanthanides - Hubbard model applied to transition metal compounds)
Insulating oxides (Excitons - d? compounds - Other closed-shell transition metal oxides)
Mixed-valence compounds
Transition metal impurities (Ruby laser - Interaction between magnetic impurities)
Magnetic insulators (Magnetic ordering of localized electrons)
Metallic oxides (Metal/non-metal transition)
Transition metal sulfides
Beyond empirical models (NiO structure: HF-DFT comparison - Configuration interaction method)

**4. Defects and Non-Stoichiometry**
Defects in oxides
Non-stoichiometric compounds (Wüstite - Uranium dioxide - Titanium monoxide - Electronic properties of non-stoichiometric oxides)
Ionic conductivity in solids

## Prerequisites

Basic knowledge of general and inorganic chemistry; crystal structures

## Teaching form

Lectures in classroom in italian

## Textbook and teaching resource

P. A. Cox “Transition metal oxides”, Oxford.

G. Pacchioni “Dispense del corso”.

## Semester

First semester

## Assessment method

Oral exam. The exam is based on the fundamental concepts of the course: synthesis of ceramic materials, their structure, physico-chemical properties, electronic structure of oxides, crystal field theory, applications (ferroelectrics, low-dimensional materials, zeolites, catalysis, glasses and cements, biocompatible materials).
The exam is aimed at verifying that the student has developed reasoning methods that enable him to solve simple problems in the field of materials chemistry.

The final score will be between 18/30 and 30/30 cum laude, based on the overall assessment considering the following criteria:
(1) knowledge and understanding;
(2) ability to connect different concepts;
(3) autonomy of analysis and judgment;
(4) ability to correctly use scientific language.

## Office hours

Office hours by appointment

## Sustainable Development Goals

AFFORDABLE AND CLEAN ENERGY