Chapter 1

INTRODUCTION

Synthesis of various inorganic materials such as metal hydroxides, oxides, phosphates, halides, chalcogenides and others with a desired structure and morphology is a subject of primary interest to materials chemists because of the potential applications of these materials in the emerging field of optoelectronics, catalysis, energy, memory storage devices and also as sensors. For the successful utilization of any material for a chosen application, it is important to have a knowledge of its crystal structure and stability, both thermodynamic and kinetic. This is because the same material exhibits different properties when it crystallizes in different structures. Crystallization in a particular structure and/or a chosen morphology depends on the method of synthesis and post synthesis treatment. In this thesis we address the various contemporary concerns of materials chemistry by the use of electrochemistry. We summarize briefly these concerns.

1.1 Contemporary concerns of materials chemistry

(i) Synthesis of new solids Just as organic chemists synthesize new molecules, solid state chemists aspire to make new solids. A new solid differs from a known one in either its composition or its structure. Thereby the synthesis of a compositionally different solid in a known structure or a solid of known composition in a new structure, both comprise legitimate synthetic goals in materials chemistry. All solids are obtained from the liquid phase—either from a solution or a melt. The thermodynamic driving force for the formation of a new phase is the degree of supersaturation of the solution or the melt. The relative supersaturation is defined as the ratio of the actual concentration of the species (C) divided by its equilibrium molecular solubility product ($K_{sp}$) under the given set of conditions.¹ All the solids reported in this thesis are made electro synthetically from aqueous baths. Thereby, controlling the degree of supersaturation by varying the conditions of electrodeposition is the central theme of this thesis.

(ii) Engineering polymorphism The phenomenon by which the same material crystallizes in many structures is called polymorphism. Of the many polymorphic modifications, only one is thermodynamically the most stable form. Other structures
being thermodynamically less stable are in a continuous state of transformation to the
most stable phase. In many instances, this transformation is very slow, often taking place
over geological time scales in nature. Such phases are variously called 'metastable' or
'kinetically stable'. As stability is a thermodynamic concept, this author prefers the more
accurate term 'kinetically not labile'. The transformation can be speeded up by imparting
energy in the form of heat, an appropriate pH, high pressure or any other means. Thereby,
solids which show polymorphism also transform from one structure to another and the
transformation is driven by both kinetic and thermodynamic factors.

Polymorphism is important in many fields such as pharmaceuticals, pigments,
foods and explosives. The solubility of different polymorphs is different and it plays a
major role in pharmaceutical action.\textsuperscript{2} Synthesizing or engineering a particular
polymorphic modification is therefore an important contemporary concern from the
scientific as well as technological point of view. Polymorphism is much less common
among inorganic materials, especially the extended (or non-molecular) solids.

(iii) Control over morphology Crystal growth takes place by the accretion and assembly
of atoms over different length scales. The packing of atoms in the sub-nanometric length
scale yields what we define as the crystal structure. The manner in which atoms assemble
over micrometer length scales defines the morphology of the crystallite. Many physical
and chemical properties depend upon the morphology. For instance, ZnO with different
morphologies shows different gas sensing and photocatalytic properties.\textsuperscript{3} Accretion and
assembly of atoms/ions/molecules over long lengths has to be controlled to obtain the
required morphology.

(iv) Oriented crystallization Crystalline solids are anisotropic, meaning that the
properties differ along different directions. Oriented crystallization promotes crystal
growth along a chosen direction, eliminating growth along others. Thereby specific $k$
dependent properties can be expressed, as opposed to that averaged over all the
crystallographic directions. Oriented crystallization can be induced by the use of
molecular templates. The interaction of a molecular template with the solid would have
shades of molecular recognition, whereby crystal growth is directed preferentially along
those crystal faces, where interatomic distances best match with the distances at the template surface.

(v) **Deposition as thin/thick films/coatings** For many device-based applications, the given material is required to be configured in the form of thin/thick films or coatings. Thin films of oxides find application in the emerging area of oxide optoelectronics. Thick films and adherent coatings find applications in catalysis, electrochemical power sources and in high temperature corrosion protection. Many techniques have been developed for the fabrication of ceramic thin films such as pulsed laser deposition, rf sputtering, electron beam etching and (metal organic) chemical vapor deposition. All these techniques require high vacuum and high power electron/ion/photon sources. Growing conformal films/coatings on curved substrates is also a challenge. Further the films could be unoriented or oriented along a specific pre-determined direction.

(vi) **Epitaxial growth** This is a process of growing films on a hard template. The template here is a single crystalline surface. The deposition takes place in an ordered fashion in such a way that the atomic arrangement of the film adopts the crystallographic structure of the substrate. This happens even when the bulk structure of the deposited material is different from that of the substrate. Epitaxial growth is one of the most important techniques to fabricate various electronic and optical devices.

### 1.2 Special features and design of electrochemical synthesis

(i) **Features** Electrochemical synthesis is carried out by passing an electric current between two electrodes separated by an electrolyte solution. The synthesis takes place at the electrode-electrolyte interface. Some features, which distinguish electrosynthesis from other synthesis methods are listed below.

(a) Electrochemical synthesis takes place at the electrode-electrolyte interface. In the interface, there is a high potential gradient of $10^5-10^7$ V cm$^{-1}$. Under this potential gradient, the reactant species are highly polarized and their reactions can potentially yield metastable products that cannot be obtained by conventional chemical synthesis.
(b) Since the electrochemical reaction takes place close to the electrode, the product essentially deposits on the electrode. As the electrode-electrolyte interface is continuous, the deposit is conformal. The deposit is in the form of a thin/thick film or a coating and the thickness can be controlled by controlling the duration of the deposition. In keeping with Hannay,4 films of thickness less than 50 Å are thin, those in the range of 50-1000 Å are thick and those in the micrometer range of thickness are called coatings. In this thesis most of the materials are electrodeposited as coatings, while nickel hydroxide is attempted to be synthesized in the form of thin films.

(c) The temperature of an electrochemical synthesis is limited by the boiling point of the electrolyte. For aqueous solutions this is 100°C. The temperature can, however, be raised by using molten salt electrolytes.

(d) The film composition can be controlled by varying the bath composition. For the synthesis of coatings of complex oxides, the deposition of each metal constituent depends on the corresponding degree of supersaturation.

(e) There are two parameters in any electrochemical reaction: the cell current and cell potential. Of the two, one can be controlled as a function of time. Thermodynamic control is exercised by choosing the applied cell potential, while kinetic control is exercised by controlling the current passed through the cell.

(f) Electrochemical synthesis is a reduction or an oxidation reaction. By fine-tuning the applied cell potential, the oxidizing or reducing power can be continuously varied. This is not possible in a chemical synthesis due to the limited availability of redox reagents of different redox powers.

(g) The experiments are easy to perform and the instruments are inexpensive.

All these features can be exploited to address the contemporary interests of materials chemistry.

(ii) Design The success of electrochemical synthesis depends upon the proper choice of the following reaction parameters.

(1) Mode of electrolysis - potentiostatic or galvanostatic
(2) Choice of the cell - divided or undivided
(3) Choice of an electrolyte
(4) Choice of an electrode - inert or reactive

(5) Temperature, pH, concentration and composition of the electrolyte solution.

In an electrosynthesis experiment, the reactant which is dissolved in the electrolyte is deposited as a solid product. Consequently, the activity of the reactant decreases as the reaction proceeds. The two important parameters that determine the course of the reaction are (i) the cell potential and (ii) the deposition current. Of the two, any one can be controlled with respect to deposition time.

In a galvanostatic synthesis (see Fig. 1.1), it is possible to control the rate of the reaction leading to deposits with good adhesion. As the activity of the reactant decreases, the cell potential changes and the variation in cell potential may lead to different products. A potentiostatic synthesis is carried out with a three electrode assembly by polarizing the electrode to a desired potential with respect to a reference electrode. In this case, the cell current decays rapidly as the reaction proceeds, due to decrease in activity of the reactant at the electrode-electrolyte interface. The concentration of the reactant in the bulk is relatively unchanged, but the rate of diffusion of the reactant from the bulk to the electrode surface is low. Potentiostatic synthesis is most likely to yield a pure single phase product, selected for by the applied potential.

In a potentiostatic synthesis, the potential to be used for the electrodeposition is not always known beforehand. Therefore a linear voltammetry is first carried out by ramping the cell potential from an initial value, $E_i$, to a final value $E_f$ (see Fig. 1.1). $E_i$ and $E_f$ correspond to potentials at which the solvent undergoes electrolysis, for instance, the hydrogen evolution and oxygen evolution potentials for an aqueous electrolyte solution. A potentiostatic synthesis can be carried out if the reaction takes place at any potential intermediate between these two values. If the reaction potential falls outside the window provided by $E_i$ and $E_f$, then a suitable electrode and solvent have to be chosen with the appropriate potential window, which includes the reaction potential. A divided cell helps to separate the product of the cathodic reaction from that of the anodic reaction and the chemical composition of the product is controlled by varying the electrolyte composition.

In an actual synthesis, one or more of these synthetic parameters may have to be empirically selected by performing a large number of trials, keeping in view the product quality.
Fig. 1.1 A schematic representation of galvanostatic (A) and potentiostatic (B) synthesis. (C) The applied potential and the current response of an electrochemical cell under a potentiodynamic operation. V, voltmeter; G, galvanostat; P, potentiostat; R, recorder; WE, working electrode; CE, counter electrode; RE, reference electrode.
1.3 Techniques The different electrodeposition techniques and other analytical techniques used in this thesis are briefly described below.

(i) Electrogeneration of base by cathodic reduction A number of reactions take place when the working electrode is polarized negative to the reference electrode.

(a) Reactions which consume $H^+$ ions such as

$$ \text{H}^+ + e^- \rightarrow \text{H}_{\text{ads}} \text{ or H}_{\text{abs}} \quad (1) $$

$$ 2\text{H}^+ + 2e^- \rightarrow \text{H}_2 \quad E^o = 0.0 \text{ V} \quad (2) $$

$$ \text{NO}_3^- + 2\text{H}^+ + 2e^- \rightarrow \text{NO}_2^- + \text{H}_2\text{O} \quad E^o = 0.934 \quad (3) $$

$$ \text{NO}_3^- + 10\text{H}^+ + 8e^- \rightarrow \text{NH}_4^+ + 3\text{H}_2\text{O} \quad (4) $$

(b) Electrolysis of water

$$ 2\text{H}_2\text{O} + 2e^- \rightarrow \text{H}_2 + 2\text{OH}^- \quad E^o = -0.828 \text{ V} \quad (5) $$

(c) Anion (nitrate) reduction reactions

$$ \text{NO}_3^- + \text{H}_2\text{O} + 2e^- \rightarrow \text{NO}_2^- + 2\text{OH}^- \quad E^o = 0.01 \text{ V} \quad (6) $$

$$ \text{NO}_3^- + 7\text{H}_2\text{O} + 8e^- \rightarrow \text{NH}_4^+ + 10\text{OH}^- \quad (7) $$

In all these cases, the pH increases close to the cathode. Nitrate reduction reaction is most effective in electrogeneration of base, as it is thermodynamically most facile and 10 moles of hydroxyl ions can be potentially generated per mole of dissolved nitrate. These reactions lead to the formation of alkali insoluble phases on the surface of the working electrode. The most commonly deposited phases are metal hydroxides. By using this technique a number of materials such as hydroxides, oxides and phosphates can be synthesized.

(ii) Electrogeneration of acid by anodic oxidation In this method the solvent, for instance water, decomposes to produce $H^+$ ions at the anode. The reaction is

$$ 2\text{H}_2\text{O} \rightarrow \text{O}_2 + 4\text{H}^+ + 4e^- $$

This reaction results in electrogeneration of acid. Acid insoluble phases are deposited at the anode. Often, a metal ion which is in the lower oxidation state gets oxidized to a higher oxidation state and deposits in the form of an acid insoluble oxide.

(iii) Alternate current/potential synthesis This method involves polarization of working electrode cathodically and anodically for time periods $t_1$ and $t_2$, respectively
called the on and off time. Using this method it is potentially possible to get layer by
layer coatings and also control orientation and morphology of the crystallites.

(iv) **In situ mass change measurement using EQCM**

Electrochemical quartz crystal microbalance (EQCM) is a very effective tool for
measuring mass changes at electrode surfaces simultaneous with the measurement of
electrochemical parameters. The microbalance is based on a quartz crystal wafer, which
is sandwiched between two electrodes, used to induce an electric field. Such a field
produces a mechanical oscillation in the bulk of the wafer. Surface reactions involving
minor mass changes can cause perturbation of the resonant frequency of the crystal
oscillator. The frequency change ($\Delta f$) relates to the mass change ($\Delta m$) according to the
Sauerbrey equation:

$$
\Delta f = - \frac{2 \Delta m \, n \, f_0^2}{A \, (\mu \rho)^{1/2}}
$$

where, $n$ is the overtone number, $f_0$ the base resonant frequency of the crystal prior to the
mass change, $A$ is the area (cm$^2$), $\mu$ is the shear modulus of quartz ($2.95 \times 10^{11}$ g cm$^{-1}$ s$^{-1}$)
and $\rho$ is the density of quartz ($2.65$ g cm$^{-3}$).5

(v) **Cyclic voltammetry**

Cyclic voltammetry consists of scanning linearly the potential of a working
electrode, using a triangular potential waveform. Depending on the information sought,
single or multiple cycles can be used. During the potential sweep, the potentiostat
measures the current resulting from the applied potential. The resulting current-potential
plot is termed as the cyclic voltammogram. The characteristic peaks in the cyclic
voltammogram are caused by the formation of the diffusion layer near the electrode
surface.5

(vi) **Potential measurement technique**

This involves measurement of the reaction potential, for instance anion exchange
reaction potential of layered double hydroxides (see Chapter 3) as a function of time. In
this method potentials are measured with respect to a reference electrode. Physical
constants can be calculated using the measured potentials.
1.4 Materials synthesized by the use of electrochemistry

(i) Metal hydroxides

Compounds $\text{M(OH)}_n$ range from the strongly basic hydroxides of the alkali and alkaline-earth metals through the amphoteric hydroxides of Be, Zn, Al, the hydroxides of transition metals to the hydroxyl-acids formed by non-metals ($\text{B(OH)}_3$) or semi-metals ($\text{Te(OH)}_3$). The alkali metal hydroxides are soluble in water and the alkaline earths less so, while most of the other metal hydroxides are insoluble in water. The larger alkali metals, alkaline earth and $\text{La}^{3+}$ hydroxides crystallize in the ionic $\text{AX}_n$ structure. On the other hand, Li, Na and smaller $\text{M}^{2+}$ ions crystallize in a layered structure. The hydroxides of K and Rb crystallize in the distorted NaCl structure, whereas the structures of the hydroxides of Cs and Tl are not known.\(^5\)

(a) Divalent hydroxides

Divalent hydroxides of the light alkaline earths (Mg, Ca) and first row transition metals (Ni, Co, Mn, Fe, Cd) crystallize in the layered CdI\(_2\) structure.\(^7\) In this type of structure the anions are hexagonally close packed and metal ions occupy alternative layers of octahedral sites. This structure is typified by mineral brucite, Mg(OH)\(_2\), which comprises a stacking of charge neutral Mg(OH)\(_2\) slabs (see Fig. 1.2). In this structure, bonding within the layer is ionic-covalent and the adjacent layers are held together by weak van der Waal’s forces.\(^8\) Mg(OH)\(_2\) is a material of great importance as the oxide residue obtained by the decomposition of this hydroxide, finds application in catalysis.\(^9\)

The hydroxides of Ni, Co, Mn, Fe and Zn which crystallize in the Mg(OH)\(_2\) structure are called as $\beta$-hydroxides. The hydroxides of Co, Ni and Mn are extensively studied because these hydroxides show redox activity,\(^10\) due to which they are used as positive electrodes in alkaline secondary batteries.\(^11\)

The hydroxides of Ni and Co also exist in hydrated forms known as $\alpha$-hydroxides. In this form, the metal hydroxide layers acquire a positive charge with the composition $[\text{M}^{II}(\text{OH})_{2.5}(\text{H}_2\text{O})_{3.5}]^{1+}$ due to the partial protonation of the hydroxyl ions. The positively charged layers intercalate anions $\text{A}^{n-}$, and yield compounds with the composition $[\text{M}^{II}(\text{OH})_{2.5}(\text{H}_2\text{O})_{3.5}]^{1-}(\text{A}^{n-})_{x/n}$.\(^{12}\) The other hydroxides with brucite structure are Mn(OH)\(_2\)
and Fe(OH)$_2$ but these metal ions are sensitive to air and get oxidized to form oxy hydroxides.

(b) Trivalent hydroxides

The metals which form trivalent hydroxides are Al, Mn, Fe, Cr and rare earths. Among all, Al(OH)$_3$ crystallizes in a layered structure in different polymorphic modifications such as gibbsite, bayerite, doyelite and nordstrandite.$^{13-16}$ Mn, Fe and Cr form amorphous gels of the hydrated sesquioxides $\text{M}_2\text{O}_3\cdot n\text{H}_2\text{O}$. The rare earth hydroxides, Re(OH)$_3$ crystallize in the UC$_3$ structure where the atoms are bonded along all the three dimensions.$^6$

Fig. 1.2 Structure of Brucite [Mg(OH)$_2$].
(c) **Layered double hydroxides**

LDHs consist of brucite-like layers in which a fraction of the divalent metal cations are substituted by trivalent ions to form positively charged layers having the composition \([M^{II}_{(1-x)}M^{III}_x(OH)_2]^{x^+}\). The metal cations occupy octahedral sites formed by hydroxyl ions. These octahedra share edges to form infinite sheets. The positive charge created on the layers is compensated by the presence of hydrated anions intercalated in the interlayer region. The general formula of LDHs is \([M^{II}_{(1-x)}M^{III}_x(OH)_2](A^{m-})_{x/2}\cdot yH_2O\), where \(M = \text{Mg, Ca, Ni, Co, Zn}\) and \(M' = \text{Al, Cr, Fe}^\text{+}\) and \(A^{m-}\) is any anion (see Fig. 1.3). The LDHs are of interest as they show many useful properties, such as high anionic mobility, anion exchange, sorption and surface basicity by virtue of which they can potentially be used as anion exchangers, catalysts and as electrodes for sensing.

![Fig. 1.3 Structure of a typical layered double hydroxide.](image)

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Basic properties of LDHs

The basic properties of the layered double hydroxides depend on the type of cation (divalent as well as trivalent) present in the layer and type of anions present in the interlayer. For instance, the Mg/Al LDH is more basic than Zn/Al, Zn/Cr and Ni/Al LDHs.\textsuperscript{25,26}

Catalytic properties of LDHs

The catalytic activity of the LDHs is dependent on the basicity of the surface and interlayer sites of these materials. The bulk basicity of these solids is different from the effective, site specific basicity that arises from the local structure of the interlayer. Consequently, methods that measure bulk properties fail to arrive at the actual effective basicity useful to carry out catalysis. On the other hand, electroactive species such as [Fe(CN)\textsubscript{6}]\textsuperscript{3-} anions can be used to probe the site specific basicity of the layered double hydroxides. The [Fe(CN)\textsubscript{6}]\textsuperscript{3-} anion was adsorbed on the surface of Zn/Al-Cl and Mg/Al-Cl LDHs. The redox potential of the resultant Prussian blue film was used to estimate the pH at the surface sites.\textsuperscript{27}

In this thesis we report (Chapter 3) a simple method to estimate the interlayer basicity of the LDHs. We intercalate the [Fe(CN)\textsubscript{6}]\textsuperscript{3-} anion in the interlayer of the LDH and estimate the interlayer pH by using the pH-dependent redox behavior of the intercalated [Fe(CN)\textsubscript{6}]\textsuperscript{3-}. The variation in the redox potential of free and intercalated [Fe(CN)\textsubscript{6}]\textsuperscript{3-} species is studied by cyclic voltammetry.

Stability of LDHs

The relative stability of a LDH in a given solvent depends upon (i) the cations present in the layer, (ii) the ion-solvent interactions in the interlayer, (iii) the electrostatic interactions between the metal hydroxide layer and the interlayer species and (iv) the hydrogen bonding strength between the anions and the hydroxyl group of the metal hydroxide layer. Therefore it is not only important to estimate the thermodynamic stability of LDHs with different metal ions, but also compare the stability of a given LDH with different anions in the interlayer.

Various methods reported in the literature to study the stabilities of LDHs are

(i) Measurement of the equilibrium constants for anion exchange reactions (Miyata method)\textsuperscript{28}
(ii) Microcalorimetric measurement of the heat of anion exchange reactions\textsuperscript{29} 

(iii) pH-metric titration method\textsuperscript{30} and 

(iv) Calorimetric measurement.\textsuperscript{31} 

Several theoretical models have been developed to calculate the heats of anion exchange reactions.\textsuperscript{32,33} 

In addition to these methods we report (see Chapter 3) a different method to study the relative stabilities of the LDHs with different anions in the interlayer relative to the nitrate-phase, by generating a potentiometric response to self-self and self-not-self anion exchange reactions. By using the potential of the anion exchange reaction, we calculate the standard free energy of the exchange reaction.

(ii) Metal oxides 

Metal oxides are ubiquitous in nature because of the high reactivity of atmospheric oxygen with the metals. The importance of metal oxides arises due to the wide range of electrical, magnetic, optical and other properties exhibited by them, by virtue of which they find applications as catalysts, sensors, phosphors and optoelectronic devices.\textsuperscript{34} 

Metal oxides crystallize in molecular, chain, layer and 3D structures, though numerically the first three classes form a negligible fraction of the total number of oxides. The majority of metal oxides have essentially ionic structure with high coordination number for the metal atom (6 or 8), the structures being in many cases similar to those of fluorides of the same formula.\textsuperscript{6} 

We give a brief introduction to the oxides which are reported in this thesis.

(a) Oxides MO 

\textbf{MgO} Magnesium oxide crystallizes in the rocksalt structure.\textsuperscript{7} It has been widely used in catalysis, toxic waste remediation, as an additive in refractories and paints.\textsuperscript{35-37} It is also used in steel manufacturing because it is highly corrosion resistant. \n
\textbf{ZnO} Zinc oxide is a n-type semiconductor with wurtzite structure and a band gap of 3.3 eV at ambient temperature.\textsuperscript{38} ZnO is of considerable interest in contemporary materials science because of its many useful applications in the emerging field of oxide
optoelectronics.\(^{39}\) In addition, it is used as a phosphor, catalyst and a general ceramic.\(^{40-42}\) Thin films of ZnO are transparent and conducting.

(b) Oxides \(\text{M}_2\text{O}_3\)

\(\text{Y}_2\text{O}_3\) Yttrium oxide crystallizes with cubic structure at ambient conditions. At high pressure, it crystallizes in a monoclinic modification. In addition to these two phases, two other polymorphs of \(\text{Y}_2\text{O}_3\) exist; they are high temperature hexagonal and disordered fluorite type phase. The cubic phase transforms to fluorite phase at 2308°C. \(\text{Y}_2\text{O}_3\) has been studied because of its wide range of applications. A dense coating of \(\text{Y}_2\text{O}_3\) is transparent and can be used as an antireflecting coating. It is also doped in \(\text{Al}_2\text{O}_3\)-based ceramics to improve ductility. An important application of cubic \(\text{Y}_2\text{O}_3\) is the red emitting phosphor, Eu-doped \(\text{Y}_2\text{O}_3\). It is an important ingredient in the manufacture of superconductors.\(^{43,44}\)

\(\text{Dy}_2\text{O}_3\) Dysprosium oxide crystallizes in cubic structure below 1870°C. At higher temperatures, it crystallizes in monoclinic and hexagonal structures. \(\text{Dy}_2\text{O}_3\) is a catalyst for the oxidative coupling of methane.\(^{44}\)

\(\text{Eu}_2\text{O}_3\) Europium oxide crystallizes in the fluorite structure, which changes to monoclinic structure at 1100°C. \(\text{Eu}_2\text{O}_3\) is widely used as a phosphor activator and in laser technology. \(\text{Eu}_2\text{O}_3\) has been used as a catalyst in organic reactions. It has selectivity and activity for ethylene and ethane formation by dimerization of methane.\(^{44}\)

(c) Oxides of the spinel structure \(\text{M}_3\text{O}_4\)

\(\text{Co}_3\text{O}_4\) \(\text{Co}_3\text{O}_4\) belongs to the normal spinel crystal structure based on cubic close packing of oxide ions, in which Co(II) occupies tetrahedral sites and Co(III) occupies octahedral sites.\(^{6}\) \(\text{Co}_3\text{O}_4\) has been extensively studied because of its potential applications in many fields, such as sensors, catalysis, memory storage, electrochromic devices and in high temperature solar selective absorbers.\(^{45-49}\)
(iii) Metal phosphates

Among the various metal phosphates, calcium phosphates have been widely studied because they are the main constituents of bone and teeth. Understanding their growth mechanism, dissolution and phase stability is of tremendous importance to the field of biomedical materials.

Calcium phosphate crystallizes in various forms, such as dicalcium phosphate dihydrate (CaHPO₄·2H₂O, DCPD), dicalcium phosphate anhydrous (CaHPO₄, DCPA), tricalcium phosphate (Ca₃(PO₄)₂, TCP), octacalcium phosphate (Ca₉(HPO₄)₂(PO₄)₄ ·5H₂O, OCP), amorphous calcium phosphate (ACP) and hydroxyapatite (Ca₁₀(PO₄)₆(OH)₂, HA). Among all the calcium phosphate phases, hydroxyapatite is the thermodynamically most stable phase. The formation of different phases depends upon the Ca/P molar ratio, pH and temperature of synthesis.⁵⁰ Among the various calcium phosphate phases, the most widely studied are the DCPD and HA.

DCPD is important for the following reasons: (1) DCPD is an acidic calcium phosphate and consequently has high solubility under physiological conditions. Thereby, it is an important precursor to the crystallization of hydroxyapatite, the inorganic component of the bone material.⁵¹ (2) DCPD is also found in pathological calcification as in dental calculi, crystalluria and urinary stones.⁵²-⁵⁶ (3) In therapeutics, DCPD is used in calcium phosphate cements⁵⁵ and as an intermediate for tooth remineralization.⁵⁶ (4) DCPD also has technological applications as a flame retardant.⁵⁷

DCPD crystallizes below pH 6.0 with monoclinic symmetry.⁵⁸ The unit cell consists of alternating bilayers stacked along the b-crystallographic axis (see Fig. 1.4). One layer consists of calcium and hydrogenphosphate ions and the other layer contains water molecules. The calcium ions are octacoordinated by six oxygen atoms of the anions and by two oxygen atoms of the water molecules.⁵⁹
Fig. 1.4 Structure of DCPD.
Hydroxyapatite (HA) is important because it is useful as a coating material for dental and orthopedic implants due to the close similarity of chemical composition and high biocompatibility with natural bone.\textsuperscript{60}

HA crystallizes in monoclinic or hexagonal symmetry depending on synthetic conditions. In the monoclinic form, rows of phosphate ions are located along the \(a\)-axis, with calcium and hydroxide ions localized between the phosphate groups. Calcium ions are placed in two triangles surrounding two hydroxide ions and in large hexagons surrounding the calcium positions. The hydroxide ions are situated either above or below the plane of calcium ions. The rows of hydroxide ions are directed alternately upward or downward. The hexagonal form of HA, generally found in biological apatites, has a structure similar to the monoclinic form, but with columns of calcium and hydroxide groups found in parallel channels. Ion substitution can readily occur in these channels and this accounts for the high degree of substitution found in natural apatites. In hexagonal HA, hydroxide ions are more disordered within each row when compared to monoclinic form pointing either upward or downward in the structure.\textsuperscript{61}

HA shows very good substitution chemistry.\textsuperscript{62} One of its hydroxyl ion can be substituted by ions like \(\text{F}^-/\text{Cl}^-\) to get flour/chlorapatite. Calcium can be substituted with cations such as \(\text{Sr}, \text{Ba}, \text{Ni}, \text{Co}, \text{and Pb}\). \(\text{PO}_4^{3-}\) ion can be substituted by the other tetrahedral anions such as arsenate and chromate.

HA is a very good adsorbent for organic molecules. It is also a good acid catalyst as it contains \(\text{HPO}_4^{2-}\), \(\text{H}_2\text{O}\) and \(\text{OH}^-\) site vacancies. The dehydrogenation of propanol and ethanol can be achieved using hydroxyapatite as a catalyst.

(iv) Metal halides

Metal halides comprise another interesting class of inorganic materials, majority of the metal halides are solids at room temperature and a relatively small number consist of finite molecules in the crystalline state. Metal halides form a very large group of compounds because most of the transition metals form more than one compound with a given halogen. For example, \(\text{Cr}\) forms all five fluorides from \(\text{CrF}_2\) to \(\text{CrF}_6\). The iodide of the Nb includes \(\text{Nb}_6\text{I}_{11}, \text{Nb}_3\text{I}_8, \text{NbI}_3, \text{NbI}_4\) and \(\text{NbI}_5\). Apart from solid solutions of two or
more halides and poly-halides, there are metal halides containing more than one halogen. Some of these compounds are ionic solids, others are apparently molecular crystals. Metal halides provide examples of all the four main types of crystal structures, three dimensional, layer, chain and molecular structure. The great majority of the halides MX, MX₂ and MX₃ adopt three dimensional and chain structures. Metal fluorides differ in structure from the other halides of a given metal except in the case of molecular halides (for instance SbF₃ and SbCl₃ both crystallize as discrete molecules) and those of the alkali metals, all the halides of which are essentially ionic crystals. In many cases the fluorides of a metal have a 3D structure whereas the chlorides, bromides and iodides form crystals consisting of layers or sometimes chain complexes.

**Halides of Cu** Copper halides (reported in Chapter 6) are p-type semiconductors and crystallize with wurzite structure under ambient conditions. These materials are of interest because of their potential applications in solar cells, catalysis and in gas sensors. The most interesting feature of the copper halides is the occurrence of a filled d¹⁰ shell of Cu(I) in addition to the s²p⁶ rare gas valence shell of the halide ion. In contrast to many compounds where the d-shell forms deep core levels with virtually no dispersion apart from the spin-orbit splitting, the d-electrons in the copper halides are part of the uppermost valence bands and therefore influence the electronic properties of these materials severely.

### 1.5 Oriented crystallization

Controlling the crystallization of inorganic solids is critical to their improved technological applications. In this regard, modifying features such as structural perfection, crystallite size, shape, and orientation are important in optimizing and determining electrical, optical, magnetic and catalytic properties.

Oriented crystallization is one of the contemporary interests of materials chemists. This kind of crystallization gains importance, if the material of interest shows different properties (mechanical, electrical and optical) with different orientation. Oriented crystallization is one of the ways to control the morphology. The crystallites nucleate and grow in a particular direction with respect to substrate and yield different morphologies.
The conventional top down method involves growing a bulk single crystal, followed by cutting and polishing in preferred crystallographic orientations and patterning. The development of bottom-up synthetic routes for the growth of preferentially oriented crystallites is of contemporary interest to materials chemists.

Crystallization in biological systems is often mediated and regulated by highly organized organic molecules. The processes of crystallization are very well controlled and the resulting crystals possess shapes and sizes that are distinctly different from those obtained under abiotic conditions. The relationship between the templating biomolecular substrate and the inorganic phase lies in the epitaxial matching of lattice spacing of specific crystal planes with some ordered arrangement of molecular units in the template.

Oriented crystallization in laboratory is achieved by using methods such as (1) the use of molecular assemblies as nucleation templates – Langmuir monolayers and self assembled monolayers, (2) solution deposition with growth modifiers – biological macromolecules, synthetic polymers and surfactant aggregates.

Oriented crystallization has been observed in thin/thick films and coatings. Several techniques have been used to get oriented films such as rf sputtering, pulsed laser deposition, chemical vapor deposition and molecular beam epitaxy. These methods require prior synthesis of the desired material, high vacuum chamber, high power laser or electron beam source. They are cost and energy intensive and one may not get the desired composition in the coating. Electrodeposition is a simple and low temperature technique for the fabrication of coatings of diverse materials on metal surfaces. By using this method it is possible to fabricate coatings on irregular objects, control the morphology and orientation by varying the deposition current, potential and bath composition.

1.6 Objectives of the thesis
The objectives of this thesis are
(1) To obtain hydroxides and oxides in the form of coatings with a porous morphology.
(2) To obtain layered double hydroxides without carbonate contamination.
(3) To use electrochemical methods to measure interlayer basicity and stability of layered hydroxides.
(4) To use electrochemical techniques to achieve oriented crystallization and to exercise control over crystal morphology.

1.7 Plan of the thesis
This thesis comprises five chapters. In the present chapter we have discussed the materials synthesized and the techniques used.
Chapter 2 has two Sections. In Section A, we report the electrochemical synthesis of macroporous hydroxide coatings and the oxide products obtained by thermal decomposition. In Section B, we report the results of cyclic voltammetry of the ultrathin Ni(OH)$_2$ coatings.
Chapter 3 has two Sections. In Section A, we report the investigation of the interlayer basicity of layered double hydroxides of Mg and Al. In Section B, we report the investigation of the stability of Mg/Al-LDH with different anions in the interlayer.
Chapter 4 has two Sections. In Section A, we report the oriented crystallization of dicalcium phosphate dihydrate and its transformation to hydroxyapatite. In section B, we report the oriented crystallization of hydroxyapatite in the presence of complexing agents.
Chapter 5 has two Sections. In Section A, we report the oriented crystallization of ZnO as a function of Zn concentration, deposition temperature and time. In Section B, the effect of a mixed water-isopropanol bath on growth direction is investigated.
Chapter 6 describes the electrodeposition of CuI.
In Chapter 7, we discuss the limitations of the work undertaken in this thesis and provide suggestions for future work in this area.

Note: Some paras in this chapter of a general nature are extracted from the thesis of an earlier coworker who worked on a similar theme.
References


