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EFFECT OF METAL CATION-SUBSTITUTION ON THE STRUCTURE AND PROPERTIES OF Mg/Al LAYERED DOUBLE HYDROXIDES

MASTER OF SCIENCE

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BOLU, DECEMBER 2023

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SAWSAN ABBAS JALOOD ALKHAZAALI

ABSTRACT

EFFECT OF METAL CATION-SUBSTITUTION ON THE STRUCTURE AND PROPERTIES OF MG/AL LAYERED DOUBLE HYDROXIDES
MSC THESIS
SAWSAN ABBAS JALOOD ALKHAZAALI
BOLU ABANT IZZET BAYSAL UNIVERSITY
INSTITUTE OF GRADUATE STUDIES
DEPARTMENT OF CHEMISTRY
(SUPERVISOR: Prof. Dr. IZZET MORKAN)

BOLU, DECEMBER 2023
(xii + 55)

Layered double hydroxides are composed by the substitution of metal cations divalent and trivalent. The trivalent metal essentially can be Al or Fe, while the divalent metals are such as Mg, Zn, and Fe. Metal cations, divalent and trivalent, can be changed. This study investigated the impact of metal cation exchange on the structure and characteristics of MgAl-layered double hydroxides.

The sol-gel method was used to synthesize the materials, and characterization studies were conducted using XRD, IR, and UV. In FT-IR analysis, the bond va\riation of each sample consisted of MgZnAl and MgZnFeAl, and MgFeAl with different amounts of metal cation concentration was analyzed and compared. XRD studies were done to determine the structural quality of the samples. UV-vis spectroscopy is used to verify the configuration of cations as arrangements within the layers while in a fluid state. Occasionally, when highly pigmented anions (such as decavanadate) are present in the interlayer, their retention groups envelop them. It was demonstrated for the first time that metal cation exchange has a clear effect on the structure and properties of layered double MgAl hydroxides.

KEYWORDS: Layered Double Hydroxides, Sol-gel processing., Mixed metal oxide.

ÖZET

METAL KATYONU DEĞİŞIMININ Mg/Al KATMANLI ÇİFT HİDROKSİTLERİN YAPISI VE ÖZELLİKLERİ ÜZERİNDEKİ ETKİSİ

YÜKSEK LİSANS TEZİ
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BOLU, ARALIK - 2023
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Katmanlı çift hidroksitler, iki ve üç değerlikli metal katyonlarının ikame edilmesiyle oluşur. Üç değerlikli metal esasen Al veya Fe olabilirken, iki değerlikli metaller Mg, Zn ve Fe gibi metallerdir. İki ve üç değerlikli metal katyonları değiştirilebilir. Bu çalışmada, metal katyon değişiminin MgAl katmanlı çift hidroksitlerin yapısı ve özellikleri üzerindeki etkisi araştırılmıştır.

Malzemeleri sentezlemek için sol-jel yöntemi kullanılmış ve karakterizasyon çalışmaları XRD, IR ve UV kullanılarak gerçekleştirilmiştir. FT-IR analizinde, MgZnAl ve MgZnFeAl ve farklı miktarlarda metal katyon konsantrasyonuna sahip MgFeAl'den oluşan her bir numunenin bağ va\riasyonu analiz edildi ve karşılaştırıldı. Numunelerin yapısal kalitesini belirlemek için XRD çalışmaları yapılmıştır. UV-vis spektroskopisi, katyonların akışkan haldeyken katmanlar içindeki düzenlemeler olarak konfigürasyonunu doğrulamak için kullanılmıştır. Bazen, ara tabakada yüksek pigmentli anyonlar (dekavanadat gibi) mevcut olduğunda, tutma grupları bunları sarmaktadır. Metal katyon değişiminin katmanlı çift MgAl hidroksitlerin yapısı ve özellikleri üzerinde net bir etkisi olduğu ilk kez gösterilmiştir.

ANAHTAR KELİMELER : Katmanlı Çift Hidroksit, Sol-jel işleme, Karışık metal oksit.

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LIST OF ABBREVIATIONS AND SYMBOLS

LDHs	**:**	Layered Double Hydroxiedes
PVC	**:**	Poly vinylchloride
2D	**:**	Two-Dimensional
TEM	**:**	Transmission Electron Microscopy
AFM	**:**	atomic force microscopy
LDO	**:**	Layered Oxide
MMO	**:**	Mixed Metal Oxide
XRD	**:**	X-Ray Diffraction
FTIR	**:**	Fourier Transfar Infrared
HTs	**:**	Hydrotalcites
UV	**:**	Ultraviolet
PXRD	**:**	Powder X-ray Diffraction

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Many thanks to my supervisor, **Prof. Dr. IZZET MORKAN**, for his assistance and guidance throughout my studies and professional progress, and for his friendship and kindness.

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To the ones that my tongue moved for the first time while I'm in their arms, letters were drawn in their presence.

For those that were just like a sawsan fragrance surrounding me, while I was an Iris for them to be proud of My mother and Father.

May you remain to be my supporters throughout my life for the ones that filled my life with their love. My brothers and sisters.

For the dear aunty and my second mother, the fragrance that unfolds from my sawsan.

For all my friends and my loved ones that supported my career path, the loyalty of your pure hearts I send my love to you.

1. INTRODUCTION

1.1 Background of Layered double hydroxides.

Layered double hydroxides (LDHs) These materials are commonly known as hydrotalcite-like materials or anionic clays (anion-exchanging), are a varied group of natural and synthetic substances that can be easily created by exposing specific combinations of metal salts to a basic environment.(LDHs) consist of many layers that include hydroxides of two or more distinct metal cations.The layers have a surplus of positive charge, which is counterbalanced via the presence of exchangeable anions (1).

Typically, the materials also include diverse quantities of water, which is bound to the hydroxide layers and/or to the interlayer anions. Regarding the instances we will examine, the metal cations are arranged in an octahedral fashion by hydroxide groups. The aforementioned criteria do not include the Ca-Al $(OH)_2$ family, whereby calcium exhibits a coordination number of 7. However, it does encompass instances, such as the later-discussed green rusts, where several cations are produced from the same element but exist in distinct oxidation states. Typically, cations are found in oxidation states of +2 and +3. However, there are some outliers to this pattern, such as the derivatives of lithium aluminum hydroxide. These materials exhibit significant interest and are used in a lot of applications, e.g., catalysts, catalyst precursors, and supports. In addition, they are good at catching anionic contaminants, like some types of nuclear waste.

They also serve as precursors for ceramics, resulting from the degradation of boulders. They are utilized as antacids and as vehicles for delivering medications, as well as additives for polymers. The final use relates to the business sector, where these materials are utilized for their capacity to counteract substantial quantities of acid produced during processes such as the which heated or degradation of polyvinylchloride (PVC), as well as their ability to inhibit the spread of flames. In the last few years, there has been a growing interest in the potential of these materials to generate self-assemble structures that include anionic surfactants. This has significant effects for the precise adjustment about characteristics (1).

The chemistry of (LDHs) has garnered significant attention in the academic community. This increased interest can be attributed, in part, to the utilization of LDHs as precursors for the synthesis of carbon dioxide adsorbents, catalysts, drug delivery hosts, fire retardant additives, cement additives , ion exchange hosts, and polymer/LDH nanocomposites (2–14).

Currently, The fabrication of low-dimensionality solids holds great significance in all basic studies, including both basic investigations and practical applications in the fields of electronics, photonics, magnetism, and mechanics The anisotropic nature of a two-dimensional (2D) nanosheet is characterized by its lateral size ranging from submicrometers to many tens of micrometers and a height of approximately one nanomete, enables its utilization as either an optimal 2D quantum system for the investigation of basic physics or as a fundamental constituent in the production of functioning solids. The assembly or organization of charge-bearing inorganic macromolecule-like nanosheets can be achieved using different solution-based processing techniques like flocculation, electrostatic sequential deposition, or the Langmuir-Blodgett method (15).

These techniques enable the production of various nanocomposites, core-shell nanoarchitectures, and multilayer nanofilms. These structures hold big promise for applications in the domains of electronics, magnetism, optics, photochemistry, catalysis. An investigation of clay mineral particle dispersions at the nanoscale scale has received significant attention because of their easily expandable properties and ability to experience surface modify using organophilic cations. The manipulation of interlayer connections has effectively resulted in the production of nanosheets made of different layered structures, such as metal chalcogenides, metal phosphates and phosphonates, and layered metal oxides (16–19).

LDHs delamination is a powerful way to make platelets that are very thin and have a positive charge. The platelets have a height of several atomic layers.These platelets have potential applications as nanocomposites in polymer materials, They could also serve as fundamental components for creating novel organic-inorganic or inorganic-inorganic nanomaterials (20–22). Unlike cationic clays e.g., laponite and montmorillonite, which can be readily separated into individual clay covers when suspended in water, LDHs provide more challenges in terms of delamination.

The layers of LDHs have a lot of charges, which makes the electrostatic interactions between them strong. The large number of anions also makes the layers very water-loving. Frequently, the presence of large interlamellar hydrogen bonding networks result in a compact arrangement of the lamellae. The intergrown platelets have a stiff spheroidal shape called the "sand rose," which makes it hard to reach a lot of the surface and stops the sheets from being peeled off in water or other nonaqueous solvents. The given data consists of a pair of numbers, specifically. Hence, the development of novel methodologies is essential to effectively achieving the separation of layered double hydroxides (LDHs) into nanosheets, characterised by either single-layer or few-layer thickness (23).

In recent years, there has been a notable surge in the number of scholarly articles pertaining to the synthesis and use of LDH nanosheets. Ma et al. (2006) conducted a concise examination of the exfoliation process of (LDHs) in formamide. Since 2006, notable advancements have occurred in the sector, although a comprehensive review study including the many production techniques and uses of LDH nanosheets remains absent from the literature. It is deemed appropriate at this juncture to undertake an examination of this domain. Our attention has been directed toward elucidating the existing techniques of delamination, their merits and demerits, as well as their prospective utilities. This paper provides a thorough examination of the latest advancements in delamination techniques.

Additionally, it discusses the essential characterization methodologies used for the examination of separation LDH monolayers or nanosheets, including X-ray diffraction (XRD), transmission electron microscopy (TEM), and atomic force microscopy (AFM). The analysis finishes by providing a summary of the existing possible uses of (LDH) nanosheets. It is crucial to acknowledge that throughout the whole of the work,(LDHs) are shortened using the following forms: M^{+2}-M^{+3}-A (where M2+ represents divalent cations, M^{+3} represents trivalent cations, and A represents the interlayer anions), M^{+2}-M^{3+} (if the anions are not stated), or LDH-A (24).

Three factors influence the primary structural characteristics of LDH: (a) The composition of the brucite-like layer, including the metal elements and atomic ratios. (b) The different types of anions that are inserted between the layers, which

can be inorganic, organic, polyoxometallates, or complexes. (c) The characteristics of the anions in the interlayer, such as their charge, size, and arrangement. Some of the things that affect the physicochemical properties of LDHs are the amount of water in the interlayer, how the brucite-like layer is stacked, and whether or not there is long- and short-range ordering. Different analytical methods can be used to identify such traits (1).

1.2 History of LDH

Initially, the examination of these materials was tackled from two distinct perspectives: mineralogy and descriptive inorganic chemistry. At first, it was not immediately apparent whether the materials were of natural or manufactured origin. The minerals belonging to the hydrotalcite and pyroaurite families have been documented since the mid-19th century and were formally characterized by 1910 (25). During the first stages of research, these compounds were initially classified as mixed hydroxides by the early writers. However, by the year 1920, further investigations led to their identification as MgAl and MgFe hydroxide carbonates. Treadwell and Bernasconi (1930) observed that the pH level necessary for the precipitation of Mg_2 in the presence of Al $(OH)_3$ was comparatively lower than the pH level needed for the production of Mg $(OH)_2$. The researchers ascribed this phenomenon to the creation of an adsorption complex; however, they did not seem to acknowledge the connection with the mineral ingredients (26).

During the late 1930s and 1940s, Feitknecht conducted a significant amount of research, as evidenced by multiple publications (27), on the synthesis of these substances through the introduction of alkali into solutions containing M^{+2} and M^{+3} ions. However, it is worth noting that Feitknecht mistakenly classified these materials as double-layer compounds, wherein alternating layers of magnesium-rich and aluminum-rich compositions were present. The author characterized the materials as having a dual-layered structure (Doppelschichtenstruktur), and our use of the phrase "layered double hydroxide" may be considered an apt but unintentional misreading of this concept. In about 1967, however, many groups accurately recognized the stratified composition as including both types of metal ions and, in doing so, acknowledged the fundamental similarity between the mineral and synthetic materials (28).

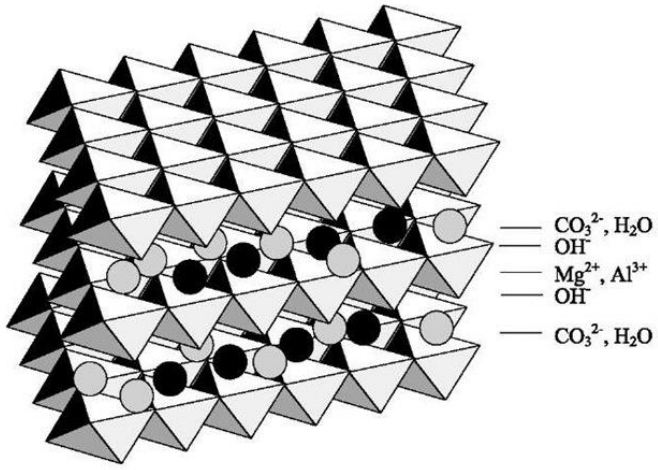
The question about the extent of ordering of metal ions inside the layers has been a subject of controversy since this era and continues to be a focus of scholarly study (29). The heat breakdown of hydrotalcite and its subsequent conversion into spinel were documented in a scientific publication in 1944 (30). The historical use of Mg-Al mixed hydroxides, often known as hydrotalcite, in therapeutic antacid applications can be traced back to at least 1960 (31). Additionally, the application of hydrotalcite fillers as flame retardants, which remains the primary and widespread usage, was officially patented in 1975 (32). In 1973, Miyata conducted a seminal study on the scope of production and anion exchange in LDH , which marked the beginning of a sustained and rapid increase in research interest in these compounds (33,34)

1.3 Structure of LDH

1.3.1 Basic Structure

The layered arrangement of LDH has a strong correlation with the structural composition of brucite, denoted as Mg $(OH)_2$. Within a brucite layer, every Mg^{2+} ion is encircled by six OH-ions in an octahedral arrangement. These distinct octahedra are interconnected by shared edges, resulting in the formation of an unbounded two-dimensional layer. The octahedron exhibits a minor flattening, where the separation among OH-neighbors on a similar edge of the layer is 0.314 nm. This distance corresponds to the crystallographic an or b spacing, specifically denoted as the length AB in Figure 1.1 Nevertheless, it is worth noting that the separation among OH-neighbors situated on opposing edges of the sheet is a mere 0.270 nm, as shown by the length CD in Figure 1.1 The bond length between magnesium and oxygen is around 0.207 nm, while the distance between consecutive layers, also known as the repetition distance or layer thickness, is measured to be 0.478 nm. This arrangement is achieved by stacking the layers on top of each other in a certain pattern (35,36).

The substitution of certain Mg2+ ions with Al^{3+} ions result in the brucite-like layers acquiring a positive charge. This positive charge is counterbalanced by carbonate anions, which are situated in the interlayer area (also known as the gallery) between the two brucite-like layers (as shown in Figure 1.1). The gallery in question also includes water molecules that are connected to layer OH and/or to the interlayer anions by hydrogen bonding. The three-dimensional arrangement shown in Figure 1.1 is held together by hydrogen bonds and electrostatic interactions between the layers and the substances inside the gallery (35,36).



Figuer 1.1 Illustration depicting the three-dimensional arrangement of the hydrotalcite structure (1).

1.3.2 Within the Hydroxide Layers

Different combos of divalent and trivalent cations have the potential to generate layered double hydroxides (LDHs). Here, Am is an intercalated anion, and the chemical formula for Mg-Al LDH is $[Mg^{2+}(1\text{-}X)\ Al^{3+}\ (X)(OH)_2]X+(An\text{-})X/n.m\ H_2O$, M^{+3} refers to a metal ion with a valence of three that is found on the platelayer. Examples of such ions include $Al^{+3,}$ $Ga^{+3,}$, Fe^{+3}, or $Mn^{+3,}$. M^{+2} refers to divalent metal ions found on the plate layer, such as Mg^{+2}, Zn^{+}, and Ni^{+2}. An- refers to the negatively charged layer that exists between layers of anions, such as CO_3^{-2}, Cl^-, and NO_3^-. z represents the quantity of water molecules situated between layers. The variable x represents the molar ratio of M^{+3} to M^{+2} and M 3+ (37,38).

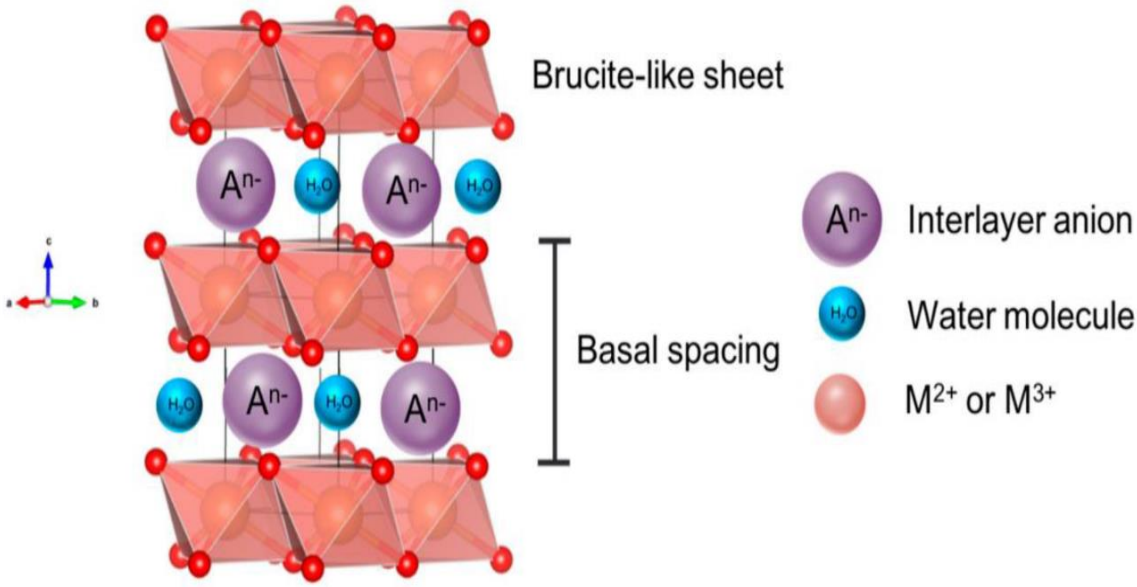


Figure 1.2 A schematic illustrating the arrangement of layered double hydroxide.

1.3.3 Between Layers

1.3.3.1 Nature of the Anions

Regarding the anions situated in the interlayer gallery, there is a wider range of options available. The range of anions that can be accommodated in LDHs is extensive, as long as they do not remove the metal ions from the hydroxide layer and possess a charge density of at least 3.0 e/nm2 in a given cross section (1). Thus far, a wide range of anions have been documented in the literature:

1- Common inorganic anions: halides $(X)^-$, CO_3, SO_4^{-2} , OH^- , NO^-_3, $Al(OH)_4^-$, or $H2AlO_3$, PO_3, HPO_4^{-2}, and PO_4(39).
2- Organic anions: carboxylates, dicarboxylates, benezenecarboxlates, alkylsulfates, alkanesulfonates (40,41) .
3- Polymeric anions: ionized poly (vinyl alcohol), poly(acrylate), and poly(styrenesulfonate), polyaniline, poly(vinylsulfonate), poly (ethylene glycol), and even polystyrene oligomer anion.
4- Complex anions: $CoCl_4^{-2}$, $NiCl_4^{-2}$ (13,42).

5- Their metal complexes and Macrocyclic ligands: porphyrin and phthalocyanine derivatives (1).
6- Biochemical anions: (a) various amino acids (1).

1.3.3.2 Orientation of the Anions

The anions exhibit significant variations in their structure, size, and charges. Nevertheless, they are uniformly accommodated within brucite-like layers. This characteristic is commonly observed in the distance between layers (referred to as d003, specifically for 3R stacking) or in the height of the space between layers (d003 minus the thickness of the brucite-like layer). Typically, anions are oriented to a certain degree in order to optimise their interaction with the surrounding environment. For instance, planar CO_3^{-2}anions are typically oriented parallel to the brucite-like layer to facilitate strong hydrogen bonding between the triple oxygen atoms and the layer's hydroxyl groups. This arrangement optimises the electrostatic interaction between CO_3^{-2}anions and the positively charged layers by minimising the gallery height, which is equivalent to the thickness of the planar CO_3^{-2}.

However, the CO_3^{-2} ions transition from a flat-lying orientation (D_{3h}) to a tilted orientation (C_{2v}) in the interlayer when the number of trivalent cations (represented by x in Ni1-xAl-LDH) grows to 0.44. This change is evident from the alteration in the infrared spectra (43).

1.3.3.3 Water in LDHs

The empty spaces in the interlayer that anions do not occupy are frequently filled with water molecules. Each hydroxyl group in the brucite-like layers serves as one such site. Typically, water molecules are bonded together by forming hydrogen bonds with the interlayer anions or with the hydroxide layer (OH) (44).

To estimate the water content in $[M^{+2}1xM^{+3}x(OH)2]$ $A_{x/c}.nH_2O$, where N represents the number of sites occupied by each anion and c represents the anionic charge,such as the case of NiMgAl-CO_3-LDH, when x is equal to 0.29, the calculated value of n is 0.565 (with c equal to 2 and N equal to 3 for CO_3^{-2} .The calculated value of 0.530 ± 0.020 is highly consistent with the value obtained from five samples. (35).

Furthermore, the study conducted by Kagunya et al. using inelastic neutron scattering reveals that the water molecules within the interlayer are not stationary but rather exhibit free rotation and movement around hydroxide oxygen sites.

Through the utilisation of Raman spectroscopy, the researchers discovered three distinct forms of structured water: (a) water that is hydrogen bonded to the interlayer carbonate ion; (b) water that is hydrogen bonded to the hydrotalcite hydroxyl surface; and (c) interlamellar water (45).

The evaporation of this water occurs within a temperature range of 120–250 °C, which varies depending on the intensity of the interactions. The presence of water molecules in the gallery can also lead to an increase in the thickness of the interlayer region, as previously discussed for LDH-SO_4 (39).Raising the temperature to 150–200°C can cause the expulsion of water while keeping the structure unaffected. Dehydrated LDHs have the ability to absorb water again when they are cooled in environments with high humidity. Furthermore, a specific quantity of water can be physically assimilated on the surface of minute crystallites. This water, which is only slightly absorbed, can be eliminated by subjecting it to a temperature of 100°C (35).

1.4 Properties of LDH

LDHs are a kind of layered compound that has interlayer anions that are negatively charged and layer hydroxides that are positively charged. Because of their ion exchange properties, they are classified as anionic clays. LDHs use interlayer materials that are very adjustable in terms of ion exchange capability, manufacturing cost and toxicity. Water treatment, solar cells , optoelectronics, catalysts , flame retardants , polymer stabilisation , packaging .Pharmaceuticals and anticorrosive applications are just a few examples of how their unique features have expanded their usefulness. In addition to their remarkable properties, LDHs can be produced with great purity using simple processes(12,46–50). LDHs are also studied as a promising novel material for enhancing the corrosion resistance of coating systems due to their ability to exchange anions, barrier effect, and self-healing mechanism. The publication delves further into their mode of action or mechanism of operation (51).

There are a few key features of LDHs that contribute to their exceptional adsorption properties: a notable porosity, a high substantial of exchangeable anions inside positively charged layers, and a structure that is impermeable to water.

They've also proven useful as anion exchangers. They can absorb a lot of negative charges because they have a lot of surface area, can exchange negative charges very well, and have interlayer gaps that can change a lot. LDHs can bind to anions in a number of ways, such as directly, through anion exchange, or by letting calcined LDH dissolve in water that already has anions in it. The reactivation of calcined LDH by hydration exemplifies its unique "memory effect." By heating them to high temperatures, oxides are produced while the interlayer anions and water molecules are removed (51).

The structure of LDHs containing intercalated anions is restored when such mixtures are rehydrated in anionic solutions. As with any high-quality adsorbent material, the ability of LDHs to rearrange their structure makes them very desirable for recycling and reuse (51,52). Layer charge density (M^{2+}/M^{3+} ratio) and the kind of intercalated anion present at the outset are two factors that affect LDHs' anion exchange capabilities.

To keep chemical species with compatible electrical charges within the layers, layered compounds are important because they can expand or contraction alongside the basal axis, which is normally perpendicular to the layers while still retaining their overall structure (a phenomenon known as a topotactic response). Layers with a positive charge, like those in layered double hydroxides and layered hydroxide salts, are stabilised by the presence of anions. On the other hand, layers with a negative charge, like those in transition metal chalcogenides and some clay minerals, are incapable of exchanging cations, and neutrally charged layers, like those in graphite and layered hydroxides, are not affected by the presence or absence of anions. The solvent contributes to the overall system stability, and cations or anions may be solvated in either the positive or negative layers (53–57).

Thousands of people perish every year in building fires across the world. The economic and social effects of this are also substantial. Therefore, a proper fire safety strategy should be used in situations where fire is a potential risk. Most

flame-retardant coatings based on nitrogen, phosphorus, and halogen are less effective as fire retardants and prevent fires, and they easily separate from the surface they are applied to due to their inferior mechanical qualities and limited ability to generate char during a fire.

Adding different LDHs to the current flame-retardant coating system may improve the mechanical and chemical properties of the coatings (54). It may be concluded that LDH is a multipurpose material with uses in various fields such as water purification, supercapacitors, lithium-ion batteries, dye-sensitised solar cells for energy conversion and storage, medicine delivery, purification of recombinant proteins, immunosensors, and DNA-based documentation. The focus of this study is primarily to investigate the mechanisms by which LDHs prevent corrosion and inhibit flames, but it also provides a short overview of their structure, characteristics, and synthesis techniques (46,58,59).

1.5 Synthetic Aspects

Layered double hydroxides exhibit a significant degree of insolubility, particularly when subjected to the relatively elevated pH levels used during their synthesis. Also, it is well known that layered double hydroxides (LDHs) are not so stable when mixed with certain anions, and there is a big difference in how stable these anions are. Therefore, in theory, the only need is to combine soluble precursor salts and, if feasible, substitute the first integrated anion with the required one. The complexity of the reality around ostensibly simple inorganic materials is much more than first perceived. However, most of the techniques used for preparation are variations on the ones listed above. For example, compounds can be precipitated by using bases, and anions can be selectively moved from precursor substances. The precise preparative details are anticipated to have a significant impact on the specific characteristics of the product, such as particle size, crystallinity, and base strength. These factors will be further discussed in subsequent sections (1).

1.6 LDHs in Nature

LDH (Layered Double Hydroxide) materials may be naturally occurring minerals or can be easily produced via synthetic methods in a laboratory setting. In natural environments, their formation may be attributed to the processes of basalt weathering or precipitation occurring in saline water sources. All naturally occurring LDH minerals have a structure that closely resembles hydrotalcite or its hexagonal counterpart, manasseite.

The bulk of these minerals may be described by the generic formula [M^{+2} (1x) M^{+3} (x) (OH)2x] x (An)x/nmH2O, where M^{+2} represents a divalent metal, M^{+3} represents a trivalent metal, and An represents an anion. In contrast to clays, it should be noted that large-scale or economically viable deposits of LDHs are not often encountered (1).

1.7 The Mothed of LDH

1.7.1 Direct Synthesis

Direct synthesis is a very prevalent technique of preparation that is extensively used in several fields. During the process, an aqueous solution with two metal ion salts, the desired anion, and a base is mixed together to make the metal hydroxide layer and make it bigger. Sodium hydroxide with a 50% concentration is especially advantageous in this context due to the common ion effect, which helps maintain its low carbonate content (as explained later). Previous studies have provided evidence that LDH materials are more likely to develop compared to a combination of separate metal hydroxides. LDH materials usually form through a stage involving aluminum hydroxide when aluminum is present as the trivalent cation. Different variations of this approach include titration under constant or variable pH conditions, as well as buffered precipitation. A fundamental constraint of this methodology is its applicability only to cases where the target interlayer anion exhibits a binding affinity equal to or greater than that of the counterion present in the utilized metal salts. Due to this rationale, the use of metal chlorides and nitrates is prevalent, while sulfates are recommended to be circumvented.

One additional constraint worth considering is that the anion intended for inclusion in the layered double hydroxide (LDH) should not easily precipitate as insoluble salts when combined with the component cations. The preparation of LDH phosphates using this approach is not feasible (60).

A range of LDH compounds have been synthesized under varying pH conditions to investigate their production. The formation of layered double hydroxides (LDHs) occurs at a pH much lower than the pH required for the formation of the most soluble hydroxide. This observation played a crucial role in first identifying LDH as a unique phase. The divalent metals (M^{2+}) that contribute to LDH formation are Zn^{2+}, Ni^{2+}, Co^{2+}, and Mg^{2+}, whereas the trivalent metals (M^{3+}) involved include Al^{3+} and Cr^{3+} (61).

Two main categories of pH curves have been observed. One observation that has been made about Cr(III)-containing LDH is the presence of a singular plateau at a pH level below the one required for the precipitation of $Cr(OH)_3$ or $M(II)(OH)_2$ (62).

This process involves the direct production of the (LDH) from a solution.The pH curve often seen has two distinct plateaus .The first plateau is correlated with the generation of the metal hydroxide with the lowest solubility, whereas the subsequent plateau is seen with the development of (LDHs) (63).

The presence of a titration curve of this kind has been documented in almost all substances that include aluminum as the trivalent metal, with the exception of copper (II). First, $Al(OH)_3$ is formed at a pH of 4. Then, this initial precipitate is changed into the final product, LDH. The materials that are made in this way start out as lumps that are not crystallized. It is hypothesized that these aggregates form by the attachment of divalent metal and extra hydroxide ions to the $Al(OH)_3$ precipitate. This is followed by rearrangement, heteronucleation of the layered double hydroxide (LDH), and dissolution of the original $Al(OH)_3$ precipitate (64).

An often-used enhancement of this methodology is precipitation in a consistent pH range, commonly known as coprecipitation. This implies that all cations precipitate concurrently in a predetermined ratio determined by the initial solution. The procedure described in scholarly literature on layered double

hydroxides entails the gradual introduction of a solution containing cations and a solution containing a base into a flask with strong agitation. The rates of addition are carefully controlled to maintain a constant overall pH. It is important to acknowledge that precipitation will take place in the mixing zone around the metal salt intake. In this area, the pH will vary significantly, and the precipitation of the least soluble metal hydroxide, at the very least, will occur rapidly. The formation of the final precipitate will occur exclusively at the designated reaction pH, provided that one of two conditions is met: either the rate of mixing surpasses the rate of conversion of the initial precipitate to LDH, or the mixture is allowed to stir for a sufficient duration, allowing any LDH formed in the mixing area to dissolve again through the process of Ostwald ripening.

The pH selected should be clearly greater than the pH needed for the synthesis of LDH while simultaneously being lower than the pH at which the divalent metal hydroxide or its basic salts would precipitate. Moreover, it is plausible that an elevated pH level may result in the inclusion of a certain quantity of hydroxide ions as a counterion, either on the surface of the particles or inside the interlayer galleries (65,66).

1.7.2 Coprecipitation in Nonaqueous Solutions

A significant proportion of precipitation reactions have been conducted in a solution that is mostly composed of water. In their study, Gardner et al. provide a detailed account of the synthesis process for (LDHs) using coprecipitation in different alcohol-based solutions. This method results in the creation of LDH materials that are intercalated with a combination of alkoxide and inorganic anions. The dispersion of this substance in an aqueous solution for an extended period of time results in the hydrolysis of the alkoxide anion and the subsequent creation of a clear LDH suspension. Upon drying, this suspension forms a thin film. Hence, this particular approach to preparation may be used in the formation of pillared anionic clays, which serve as precursors for the production of clear LDH film (67).

1.7.3 Anion Exchange Within an LDH Precursor

The following is the order of preference of interlayer anions in layered double hydroxides (LDH), which determines their exchangeability:

NO_3^- <, Br^- <, Cl^- <, F^- <, OH^- <, MoO_4^{2-} <, SO_4^{-2} <, CrO_4^{-2} <, $HAsO_4^{-2}$<, HPO_4^{-2} <, Naphthol Yellow $^{-2}$ <, and CO_3^{-2}.

The observed sequence may be attributed to the influence of charge, charge density, and hydrogen bonding. One notable implication is that an anion with less binding affinity may be effectively substituted with an anion that has a stronger binding affinity. This substitution process can be easily achieved by agitating the layered double hydroxide (LDH) material containing the target anion in a solution that contains an excess amount of the substituting anion. This technique often employs LDH nitrate and chloride as primary reagents. This simple approach has proven effective in intercalating anions of both organic and inorganic origin, which exhibit diverse sizes, shapes, and charges, into LDH.

Nevertheless, we have discovered, to our first astonishment, that the entire eradication of the distinctive nitrate signal proves to be really challenging, even when using the much more tightly bound carbonate anion. It is postulated that some nitrate monoanions may exist in an isolated state inside the lattice. Consequently, we contemplate if chloride, which lacks a distinctive indicator of such behavior, has a similar tendency (68).

There are a limited number of significant limits on this approach. The use of poorly held anions, such as iodide and perchlorate, poses challenges. For the required material to develop, it is essential that the area per unit charge of the integrated anions does not exceed the area per unit charge of the LDH sheet. The aforementioned limitation is more stringent than it first seems, since some anions, such as metal cyanide complexes, possess hydrogen-bonding prerequisites that result in a larger spatial need than anticipated (69).

The anion exchange technique is extensively used in the synthesis of pillared clays. The term "pillaring" refers to the structural impact exerted by a bulky and strongly charged anion on the layered double hydroxide (LDH) structure. In an ideal

scenario, the anion assumes a perpendicular arrangement, positioned between two layers of metal hydroxide. This arrangement serves to enhance the surface area and pore volume that are often associated with (LDHs). Polyoxometallates are widely used as pillaring agents for anionic clays (70).

The selection of these materials is based on their robust nature and highly charged characteristics, which are known to possess significant catalytic activities. The strength of the material contributes to the ability of (LDH) to accommodate significant gallery heights. Additionally, the charge of the LDH aids in expanding the interlayer space, resulting in an increased amount of unoccupied area between anions. The preparation of pillared anionic clays might present challenges due to the occurrence of side reactions, the influence of various circumstances on the nature of the pillar, and potentially the significant gallery height. Due to this rationale, several laborers have opted to indirectly include the polyoxometallate pillars by means of displacing a vertically elongated organic pillar, such as terephthalate (71).

1.7.4 Glycerol-Effected Exchange

This particular approach represents an additional iteration of the exchange reaction that has been previously examined. In this experimental procedure, glycerol or another glycol is added to a solution containing LDH carbonate. This addition is meant to make it easier for carboxylate anions to enter the LDH carbonate interlayer by first making the spaces between the hydroxide layers bigger. The precise mechanism behind this response remains partially elucidated. One hypothesis posits that glycerol or glycol has the ability to permeate the interlayer, resulting in its expansion. This phenomenon results in a reduction in the strength of hydrogen bonding between the carbonate anion and hydroxide layers.

The diminished strength of the bond decreases the ability of the carbonate to withstand substitution by an alternative anion. According to the second hypothesis, the reaction involves the interaction between a glycerolate anion carrying a negative charge and the carbonate present in the layered double hydroxide (LDH). This interaction leads to the displacement of the carbonate by the pillaring carboxylate species. In actuality, it is likely that a confluence of processes takes place (72).

The experiment was conducted utilizing two distinct reaction conditions, with the only difference being the temperature at which the glycerol treatment was performed. Using glycerol as the reactant in an exchange process at room temperature results in a small increase in the basal spacing. This is because carboxylate anions are absorbed. Under conditions of increased glycerol temperature, the same process yields material exhibiting a much greater augmentation in basal spacing. The observed discrepancy is likely attributed to the distinct configuration of the carboxylate anion, namely a monolayer vs. a bilayer arrangement (1).

1.7.5 Preparation from Oxides and Hydroxides

There are two preparation techniques that are associated with the creation of LDH from oxides and hydroxides. The first phenomenon refers to the accidental occurrence seen in antacids (73). The process under consideration involves the addition of water molecules to metal oxides and/or metal hydroxides in the presence of an anionic species. The alternative variant employs a memory attribute inherent in LDH materials. The approach used in this study involves the calcination of (LDH) materials that consist of a thermally unstable interlayer anion. Subsequently, the resultant amorphous oxides are rehydrated in the presence of the required anion (74,75).

The process of hydrating metal oxides and hydroxides has been used for the synthesis of (LDHs), exemplified by the production of Mg/Al LDH in antacid formulations. The reaction is postulated to occur via a dissolution or precipitation mechanism, likely including heteronucleation in one of the first hydroxide phases. The conversion of oxides or hydroxides leads to the development of (LDHs), which results in an excess hydroxide group for each trivalent metal integrated into the LDH structure. The interlayer hydroxide, which exhibits a high degree of basicity, has the ability to undergo a reaction with carbon dioxide or other weak acids (1).

One approach that is sometimes denoted as the memory effect of LDH is used. The methodology involves the application of heat to a layered double hydroxide (LDH) compound that contains an anion susceptible to thermal degradation. Subsequently, the amorphous oxide obtained is subjected to rehydration in the

presence of the intended replacement anion, leading to the formation of a novel (LDH). The selection of the initial substance and the temperature of the calcination process are two significant aspects to consider in this methodology. The initial substance used should consist of an anion that is susceptible to thermal degradation, and it is crucial to carefully regulate the calcination temperature to prevent excessive heating that might lead to the creation of spinel, a compound known for its resistance to rehydration (1).

1.7.6 Preparation by Reaction of Metal Oxides/Hydroxides with Salts

The deposition of metal ions onto an oxide surface has significance in the fields of colloidal chemistry, surface science, and geochemistry. Hydrotalcite-like materials have been shown to emerge by the process of impregnating a metal ion onto a metal oxide or hydrogen surface using a metal salt solution (76–79). The first stage of the process likely involves the generation of an electric charge on the surface of the metal hydroxide as a result of dissociation. In a study conducted by Caillerie and Clause, the formation of LDH was found in β-alumina that was impregnated with Ni(II) and Co(II) ions. Similarly, Mascolo and Marino showed that alumina gel absorbed Mg(II) ions, resulting in the formation of $[Mg1xAlx(OH)_2]$ x $[xOH(0.81x)H_2O]$, where x ranged from 0.23 to 0.33. In their study, Nayak et al. (year) observed that alumina gel exhibited the capacity to adsorb Li(I) ions from a LiOH solution, resulting in the formation of the hydrotalcite analog $LiAl_2(OH)7{\cdot}2H_2O$ (77).

1.7.7 So-Called Homogeneous Precipitation

An interesting thing that happens called homogeneous precipitation is that one of the reactants slowly turns into a very insoluble substance where it was. This process helps prevent excessive supersaturation during the mixing of reactants, leading to a decrease in the number of nuclei formed. Consequently, this results in the production of larger particles with improved crystalline structure. The aforementioned reasoning has been used in the synthesis of LDH carbonates by the gradual hydrolysis of urea. This process results in the production of a base, namely ammonia, and hydrogen carbonate, which exist in equilibrium with ammonium carbonate (80).

The LDH exhibited a formation characterized by euhedral platelets with a crystallographic orientation. However, it is evident from pH titration investigations that the underlying process included the gradual dissolution of an initial precipitate of aluminum hydroxide. Nevertheless, the reaction may be considered homogeneous as all the required chemicals for the precipitation of LDH are present, either directly or as a result of an internal reaction within the initial reaction mixture.

The approach described in this study was used for the precipitation of Co/Al LDH, resulting in the formation of hollow aggregates composed of platelets. This phenomenon may be attributed to the process of heteronucleation occurring on the originally generated aluminum hydroxide, which subsequently undergoes redissolution. In theory, the generation of Zn/Cr LDH by genuine homogeneous precipitation should be feasible. However, the occurrence of complex formation between metal cations and the hydroxide precursor has consistently hindered our experimental results (1).

1.7.8 Precipitation via Aluminate

All of the above ways to get to LDHs that use aluminum as the trivalent metal have been shown to work by making solid Al $(OH)_3$. This poses evident challenges in achieving precise control over the resulting product throughout the preparation process. In recent studies, researchers have conducted investigations that make use of the amphoteric properties of Al $(OH)_3$ in order to precipitate LDH straight from a solution without the need for Al $(OH)_3$ nucleation. In the process of synthesizing (LDHs) using the aluminate route, various aluminum compounds such as aluminum salt, aluminum hydroxide, or aluminate are initially reacted with an appropriate amount of base. For instance, if the desired LDH product is of type M(II)2Al $(OH)_6X$, six hydroxide ions are added for each aluminum ion. Subsequently, M(II) is introduced into the reaction mixture, either in the form of a salt or carbonate , or as an oxide or hydroxide (81).

The observed pH graph for this titration exhibits endpoints that are associated with the generation of aluminum hydroxide (Al $(OH)_3$), aluminate, and (LDH). This particular approach to formation results in the direct production of LDH from a solution without any intermediate solid phase involved. The metal hydroxide layer

of the result exhibits a higher level of organization and a slightly reduced surface area in comparison to LDH synthesized using other techniques. This conclusion is supported by many analytical techniques, including infrared spectroscopy, powder X-ray diffractometry, scanning electron microscopy, and MAS ^{27}Al and MAS ^{35}Cl NMR (81–84).

1.7.9 Preparation from Metals

The synthesis of LDH from metal precursors, as opposed to metal salts, requires an extra oxidation process, and is hardly used. One of the most often seen materials produced during this process is commonly referred to as "green rust" (85). This phenomenon arises due to the process of metallic iron undergoing oxidation in water, leading to the creation of Fe+2 and Fe+3 ions. It has significant relevance in the context of corrosion (86). These types of reactions may be useful when conducted in deuterated water (D_2O) for the synthesis of multilayer double deuteroxides with specific applications, For example neutron diffraction investigations (1).

1.8 Postpreparative Treatments

Usually, the steps used to make LDHs result in materials with few crystals and layers of jumbled metal hydroxides. In situations where there is a need for enhanced uniformity and crystallinity, the LDH is often modified using post-preparative procedures. These procedures include subjecting the precipitate to aging at or above the ambient temperature, such as by gently refluxing it through heating. The process of aging is believed to be driven by Ostwald ripening, a phenomenon where bigger and more well-formed crystallites develop by consuming smaller particles in a solution via dissolution and reformation processes.Furthermore, as part of the aging process, LDH materials undergo thorough washing after creation to eliminate any surplus ions present in the solution that may potentially undergo further reactions with the material (87,88).

Hydrothermal treatments and microwave treatments are methodologies used for the processing of LDH, which is created using one of the preparatory procedures discussed above rather than being considered as distinct ways of preparation. While

there are variations in the excitation methods used in these two procedures, the ultimate result remains consistent: an enhancement in the crystallinity of the LDH material. The process of hydrothermal treatment promotes the dissolution and recrystallization of layered double hydroxides (LDHs) using heat during the LDH production process.

The temperature used for this technique is determined by the intended LDH (Layered Double Hydroxide) formation. For instance, at temperatures over 120°C, Mg_2Al $(OH)_6A$ transforms into Mg_3Al $(OH)_8A$ and Al $(OH)_3$. The precise mechanism by which microwaves interact with the reactants during the creation of (LDHs) remains uncertain. However, it is widely accepted that this particular interaction involves the transfer of energy, leading to fast heating via the processes of resonance and relaxation. The outcome of microwave treatment yields a highly crystalline material with a shorter duration compared to traditional hydrothermal treatments (1,89).

1.9 Industrial Production

The synthesis of (LDHs) has been extensively investigated and documented in more than 50 patents. The claims made are specific variations on general methods that have already been explained. These include coprecipitation , anion exchange , synthesis from oxides and hydroxides , the reaction of metal oxides or hydroxides with a salt, and precipitation through aluminat (90,91). The primary substance discussed in this context is Mg/Al LDH carbonate. Nonetheless, other anions, including heavy metal complexes, anionic surfactants, alcoholates, halides, and phosphates, have also been reported. LDH may be generated by the controlled introduction of $CaOH_2$ and AlCl3 into saltwater (92).

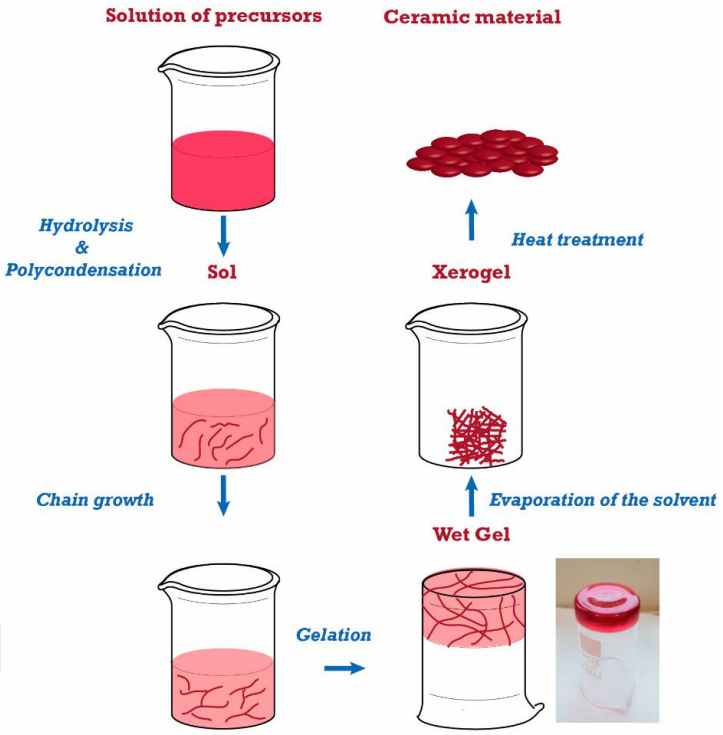
1.10 SOL/GEL Chemistry

1.10.1 Fundamental Features

Using colloidal solutions (sol) as starting ingredients, sol-gel chemistry provides a versatile method for creating high-tech materials including organic-inorganic hybrids, ceramics, and glass (93). Producing monoliths, coatings, foams, and fibres, among other shapes, does not require the use of powder intermediates or high-priced processing technologies like vacuum techniques (93,94).

Hydrolysis and condensation of metal alkoxides gave rise to the first "sol-gel" materials. Ebelman created the first metal alkoxide by reacting silicon tetrachloride ($SiCl_4$) with alcohol, and then noticed that $SiCl_4$ gelled when exposed to air. Despite this, for a long time, little practical interest was shown in these materials. Geffcken didn't figure out that alkoxides might be used to make oxide films until 1930 (95).

The German "Schott glass company" eventually adopted and refined this method, as detailed in an outstanding study by Schroeder (95). Long-term research has been conducted on the formation of inorganic gels from aqueous salt solutions. To support the idea that silica gel consists of a solid structure with uninterrupted porosity, Graham demonstrated the possibility of replacing water in silica gel with organic solvents (96). In 1930, following extensive work by Hurd, who demonstrated that silica gels were required to be created by a silicon polymer skeleton enclosing a liquid phase, this description was generally accepted. The sol-gel method is a low-temperature synthesis methodology that permits precise manipulation of the final product's microstructure during the preparation of complicated inorganic materials like ternary and quaternary oxides (97).



Figuer 1.3 Illustration depicting the sol-gel method.

- A technique for making a precursor solution.
- A formation of a "sol" by the partial condensation of alkoxides and hydrolysis
- The polycondensation of hydrolyzed precursors is responsible for the gel's formation.
- Drying. Because of the collapse of the porous structure due to the evaporation of the solvent, the gel transforms into a dense "xerogel" (or an aerogel, for instance, by supercritical drying).

The process of calcining materials to make them mechanically stable an ageing process may be included after gel creation since chemical processes continue long after gel formation, altering the gel's composition, structure, and characteristics. The steps in Figure 1 are just an example and are not meant to be comprehensive. The duration of each step and how it adapts to the demands of the application are both flexible. Controllable factors in the sol-gel process include 1. precursor concentration and type, 2. solvent nature, 3. solution pH, 4. additive type

and concentration uch as catalysts, surfactants, and structure-directing agents, 5. pre-heat treatment, 6. ageing time and 7. post-heat treatment (95).

1.10.2 Gelation: Hydrolysis and Polycondensation

To grasp sol-gel chemistry, one must first understand the reaction processes responsible for the gelation process: hydrolysis and condensation reactions. In the hydrolysis process, it is thought that a nucleophilic substitution mechanism is at work, which causes the alkoxy group to switch places with the hydroxy group.

$$\equiv \mathbf{M} - \mathbf{OR} + \mathbf{HOH} \leftrightarrow \equiv \mathbf{M} - \mathbf{OH} + \mathbf{ROH} \ (\mathbf{1})$$

$$\equiv \mathbf{M} - \mathbf{OH} + \equiv \mathbf{M} - \mathbf{OH} \leftrightarrow \equiv \mathbf{M} - \mathbf{O} - \mathbf{M} \equiv + \mathbf{HOH} \ (\mathbf{2})$$

$$\equiv \mathbf{M} - \mathbf{OH} + \equiv \mathbf{M} - \mathbf{OR} \leftrightarrow \equiv \mathbf{M} - \mathbf{O} - \mathbf{M} \equiv + \mathbf{ROH} \ (\mathbf{3})$$

Figuer 1.4 The sol-gel process of an alkoxide M(OR)4 has three primary reaction steps: 1) hydrolysis of an alkoxy group; 2) condensation of two species containing OH groups; 3) mixed condensation of a species containing an OH group and a species containing an alkoxy group (102).

An alkoxide of element M would have the formula M(OR)4, where R stands for the alkyl group. Alcohol (ROH) is a superior leaving group because the nucleophilic addition of water is followed by a proton transfer (93,94,98). Therefore, the nucleophilicity of the entering group and the + charge on element M dictate the thermodynamics of this reaction. The stability of the leaving group, the electron-donating capabilities of the OR group, and the electronegativity of the element are all factors in determining the former. However, the reaction rate improves with increasing (N-z), where N and z represent the coordination number and the charge of element M, respectively (93). According to a nucleophilic substitution mechanism, the length of the alkyl chain of the alkoxide (steric encumbrance) also plays a role in the rate of the reaction. Alcohol association and oligomerization are not seen in transition metal alkoxide, which is in stark contrast to the most prevalent silicon alkoxide (N = z) (93).

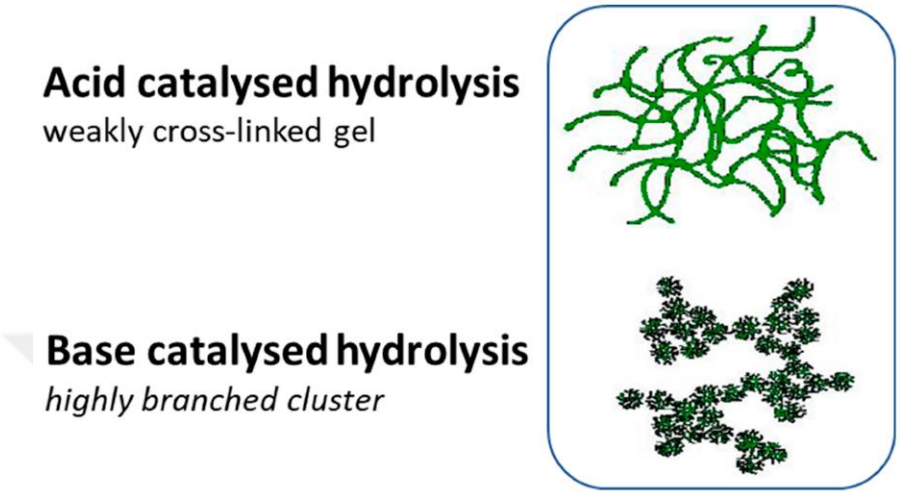
The polycondensation process takes place simultaneously with the hydrolysis reaction, and it involves the partly hydrolyzed alkoxide molecules reacting with either another OH-containing species, removing water (reaction 2 in Scheme 1.4), or with an alkoxy group, creating an alcohol molecule (reaction 3 in Scheme 1.4). Gel is a three-dimensional polymeric network formed when clusters bond together as a result of hydrolysis and polycondensation processes; at this point, viscosity is found to rise dramatically (93). In the synthesis of metal oxides, the M-O-C bonds are often strongly polarised, and hydrolysis rates are high because of the high electronegativity of the oxygen relative to the metal. Hydrolysis rates are lower for non-metal alkoxides (such as Si, P, and Ge).

Gelation may occur at various periods in multicomponent systems (mixed oxide production) because of the varying hydrolysis rates of the precursors, resulting in phase separation phenomena caused by homo-condensation reactions rather than hetero-condensation. Using reaction inhibitors (like chelating agents) to slow down the hydrolysis rate of the most reactive precursor and a catalysed (acidic or basic) pre-hydrolysis to speed up the hydrolysis rate of the less reactive precursor can solve this issue. Another option is to employ double alkoxides with well-defined stoichiometry (93,94,98). Factors influencing the condensation reactions and hydrolysis can be used to fine-tune the gel properties and, thus.

The characteristics of the substance during all subsequent stages of processing. The sol-gel approach is preferred over other preparation techniques because of the ease with which these parameters may be adjusted.

Since the gel's precise definition is still up for debate, it's worth recalling Nijenhui's more philosophical take on the matter: "A gel can be classified as such unless there is evidence to demonstrate otherwise."(2). In the laboratory, gel time is defined as the amount of time it takes for the solution to get so thick that a magnetic stir bar can no longer be used to keep a vortex in it during the sol-to-gel transition. The amount of water present and the nature of the catalysis have major impacts on its structure. Silicon dioxide made from acidic "sol" has a structure of linear polymers with few crossed links. Silicon dioxide made from basic "sol" has clusters with many branches. This is due to the competitive influence of pH-

dependent hydrolysis and condensation reaction rates. Since the condensation and hydrolysis rates are governed by steric hindrance factors, the choice of alkoxy groups can also govern the reactivity of silicon alkoxides, $Si(OR)_4$ (99,100).



Figuer 1.5 The gel's structure results in both acidic and basic-catalysed hydrolysis(101).

1.10.3 Converting A Wet Gel into A Dry Solid

A moist gel produced by the hydrolysis and polycondensation of the alkoxide is dried and then treated with the proper heat in order to achieve the material's desired properties. A moist gel is dried by heating it to a temperature of about 100 °C, at which point the physically bonded water and alcohol are released. Evaporation may turn a wet gel into a dry one, but the process causes the gel's primitive porous backbone to distort, which is commonly followed by the production of "cracks" (93,94,98). Chemical factors, e.g the condensation reaction, and physical impacts, like capillary pressure, are the primary causes of shrinkage. If there was a consistent pressure throughout the liquid, the lattice would be evenly crushed, and cracking would be prevented. However, due to the gel's limited permeability, a pressure gradient is created, and the disparity in the rate of contraction between the interior and outside of the gel is what causes the fractures to develop.

In the absence of a structure-guiding agent, the outcome of this uncontrolled drying is termed xerogel, and it has a disorganised porosity. The effects of warping and cracking may be dampened by ageing the gel. Wet gels undergo changes in their physicochemical characteristics as a result of the ongoing chemical events that initiate gelation. Ageing lessens the following shrinkage during drying because the development of new crosslinks causes shrinkage (syneresis) while also increasing the modulus and viscosity of the gel (93,94). When the pore liquid in a gel is replaced by air, a mild contraction of the matrix results in aerogel. The smallest effect on the porous structure is typical when this is attained in the supercritical drying (SCD) state. Freeze drying is another method for producing porous materials; the resulting cryogel often falls in the porousness range between xerogel and aerogel. What comes next, in terms of heat treatment, is determined by the final product. Dry gel is often heated to between 300 and 500 °C to drive off any lingering organics. While calcination often produces more mechanically stable materials, sintering may enhance density while decreasing pore volume and surface area (101).

1.10.4 Advantages and Disadvantages of Sol/Gel

With increased topcoat-with-substrate bonding, when substances are in a gel condition, they are more amenable to being shaped into intricate patterns. The sol-gel transformation uses ceramic oxides as a precursor, which are dissolved in a suitable solvent to produce high-purity products. The suggested sol-gel synthesis pathway for LDHs shows advantages in terms of ease of use, product homogeneity and crystallinity, accuracy, cost-effectiveness, and amenability to the production of a variety of LDH compounds (102).

The main problem with the sol-gel method is that the LDH that is made when the corresponding MMO is rehydrated gets mixed with OH, even if there are no other anions (except for CO_3) in the solution. Since OH and CO_3 have a great affinity for the double-metal hydroxide layer, Replacing hydroxide and carbonate with other anions, including functional ones, is a challenging task. The process of removing carbonate from commercially available Mg3Al-CO3 hydrotalcite using a solution of HCl and NaCl acid-salt was explained. It's safe to presume that Mg2Al-

OH LDH can have its chloride replaced by hydroxide using the same or a similar procedure (103,104).

1.11 Mixed Metal Oxide (MMO)

The composition of mixed oxides obtained from roasted LDHs produced by direct and indirect methods is a fascinating subject, as the conditions of reformation can influence both the characteristics of the oxides as well as the composition of the solid. The surface areas of roasted LDH materials or mixed metal oxides are typically high. Dehydroxylation of LDHs with various chemical compositions during the calcination resulted in the crystallization and interstratified structure of metal oxides, which led to the production of mesopores and an increase in both the specific surface area and the capacity for sorption (105). It's interesting to note that the produced MMO can occasionally maintain the LDH precursor's shape and also demonstrate effective recycling of the used adsorbent. It has been discovered that the kind of cationic that is partially injected into the M2+ position affects both the structural and morphological characteristics of the produced mixed metal oxides as well as the thermal decomposition conditions of LDHs (105).

1.12 Practical Applications of LDHs

The investigation into the applications of LDHs is continuously broadening. Currently, LDHs have been extensively utilized in several fields, including sorbents, electrocatalysts, energy storage, medication delivery, catalytics, memory, sensors, and photocatalysts. Nevertheless, a significant number of applications are constrained in their effectiveness because they cannot reach the inner surfaces of the host layers.

Table 1.1 Practical applications of LDHs.

Type of LDH	LDH synthesis method	Application of LDH	References
MgAl	Co-precipitation	Drying	(106)
MgAl-LDH	Urea method	Water treatment sector	(107)
Mg/Al (M= Mn, Co, Ni, Cu)	Sol-Gel	transition metal substitution effects	(108)
Zn/Al, Zn/Fe, Zn/Cr	Co-precipitation	Effect of M^{3+} Ions	(109)
Zn/Al-LDH SiO2	Sol-gel	Drug delivery	(110)
FeCoNi-LDH	Ion-exchange	Catalytic	(111)
C/NiFe-LDH	Hydrothermal	Adsorption	(112)
ZnNiCr-LDHs	Microwave Hydrothermal	Adsorption	(113)
Nb-NiFe-LDH	Salt-oxide	Catalytic	(114)
ZnAl-LDHs	Reconstruction	memory, sensor	(115)
NiAl-LDH/g-C3N4	Urea method	Photocatalyst	(116)

2. AIM AND SCOPE OF THE STUDY

The aim of this work was to study the Effect of Metal Cation-Substitution on the Structure and Properties of Mg/Al Layered Double Hydroxides. We also aimed to decide the changes in the their structure, composition, and properties when metal cations are replaced in layered double hydroxides (LDHs), especially in the Mg/Al system. Sol-gel preparation method was used for that purpose.

Examination of alterations in the arrangement of layers, the distance between layers, and the characteristics of the crystal lattice were also one of our work aim. Utilise methodologies such as X-ray diffraction (XRD) to examine alterations in the structure, FT-IR analysis, the bond variation of each samples consisted MgZnFeAl,MgZnAl and MgZnFe with different amount of metal cation concentration will be analyzed and compared. UV-vis spectroscopy is used to check how the cations are arranged as groups in the layers when the substance is fluid. Occasionally, when highly pigmented anions (such as decavanadate) are present in the interlayer, their retention groups envelop them.

3. MATERIALS AND METHODS

3.1 Materials

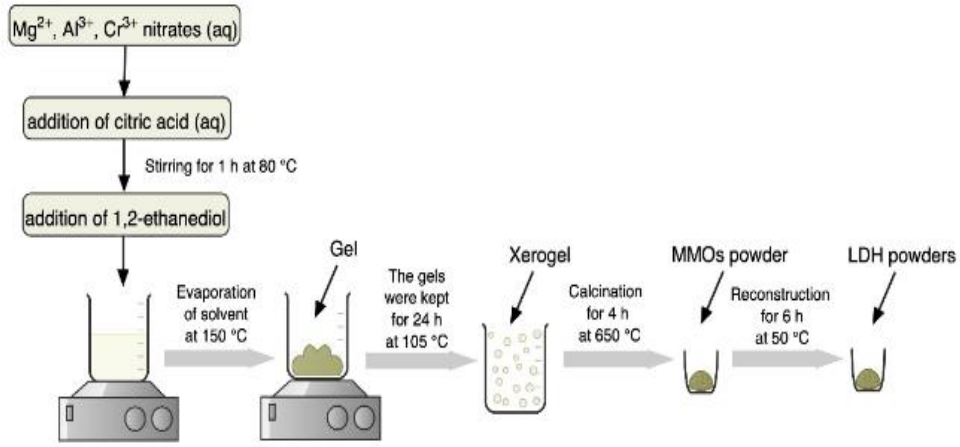
The anion modifications and production of LDHs were conducted using the following ingredients: Mg $(NO_3)_2 \cdot 6H_2O$**,** Zn $(NO_3)_2 \cdot 6H_2O$, Fe $(NO_3)_2 \cdot 3H_2O$ and $Al(NO_3)_3.9H_2O$,($C_6H_8O_7.H_2O$, 0.2M) **,** ($C_2H_6O_2$, 99.0%] .Deionized and decarbonized water were utilized for the purposes of synthesizing compounds, preparing solutions, and cleansing the end products.

Table 3.1 DATA OF LDH

LDH	Mg	Zn	Fe	Al	
1	2.94 M	0.01 M	0.05 M	1.00 M	
2	2.94	0.02	0.04	1.00	
3	2.94	0.03	0.03	1.00	
4	2.94	0.04	0.02	1.00	
5	2.94	0.05	0.01	1.00	
6	2.94		0.06	1.00	
7	2.94	0.06		1.00	

3.2 MgZnFe/Al LDH synthesis

Mg $(NO_3)_2 \cdot 6H_2O$, Zn $(NO_3)_2 \cdot 6H_2O$, Fe (NO3)2·9H2O, and Al $(NO_3)_3.9H_2O$ (3:1 molar ratio) were dissolved in 50 ml of distilled water, and then a solution of citric acid ($C_6H_8O_7.H_2O$, 0.2M) was added and continued stirring for 1 h at 80 C^o. After 1 hour, 2 mL of ($C_2H_6O_2$, 99.0%) ethylne glycol was added under continuous stirring at a temperature of 150 C^o until the solvent evaporated completely. The translucent gels that were formed were subjected to a drying process at a temperature of 105 C^o for a duration of 24 hours. After grinding, the mixed metal oxides (MMO) were synthesised by subjecting the gels to a temperature of 650 C^o for a duration of 4 hours. The formed MMO powders were rehydrated in 30 mL of deionized water under continuous stirring at 50 C^o for 6 hours. After the rehydration process, the final resulting gel was dried at 70 C^o for 12 hours, and LDH powder was obtained.



Figuer 3.1 Diagram of the sol-gel preparation of$Mg_3Al_{1-x}Cr_x$ layered double hydroxides (LDHs).

3.3 Characterisation of LDH

3.3.1 FTIR Spectroscopy

Fourier transfer infrared (FTIR) spectra were recorded on PerkinElmer Model: spectrum TW0 Serial No:98548 Instrument Performance Verificatlon C.S.E. Sıgnature: Berak. k4Tm B.K Date:01.DEC 2014 Next OQ Due Date :01:DEC 2015. The specimen was combined with desiccated KBr of spectroscopic quality and compacted into a disc.The use of KBr, a small amount of it is taken in a dry, pure form, free of impurities, about 0.1500 mg, and grinded with the sample to be measured, with an amount estimated from 0.0010mg, using a ceramic powder, and pressed with high pressure about 3× 10 mPa in the form of a very thin tablet, the thickness of which does not exceed 1 centimeter, and it is placed in the designated place For cells of solid materials, The spectrum was recorded between 400 and 4000 cm1., and the use of the potassium bromide method has disadvantages, including that potassium bromide absorbs some moisture during grinding, and it interferes with the spectrum.

Figuer 3.2 Setaram (Sensy -Sevo) Apparatus.

3.3.2 Powder X-Ray Diffraction (XRD)

X-rays taken in the lab Because of the ease with which both temperature and environment may be controlled in the laboratory, in situ X-ray diffraction provides a low-cost and very practical tool for researching high-temperature solid-state changes such as gel crystallization and aging. Diffraction measurements can be used to infer a variety of properties of sol-gel transformations, such as the rate of amorphous or crystalline phase digestion, the rate of product crystallization, the rate of solid-solid transformations, and the crystallinity evolution of the final product. The impact of synthesis factors such as gel composition, templates, pH, temperature, and time may also be investigated. Moreover, in the case of short-lived entities that are structurally important and stable at high temperatures, in situ X-ray methods provide a chance to study the production of precursors and intermediates. Crystallization kinetics are investigated by tracking the integrated intensities of certain reflections over time. The rate constants and reaction orders may be calculated by using the Avrami equation to model the development of a single reflection of interest (139).

To determine the crystal structures and to calculate the lattice parameters of the phases, PXRD analysis of synthesised compounds was performed with an X-RAY diffractometer (Rigaku) (Model: Mu l Tiflex 2kw) (Cat No.: 2013F303),

(power: 200 VAC, 1 30A, 50Hz) (Ser No. D02759N) (Date: Nov. 2006, Rigaku Corporation) (Made in Japan) using primary-beam Cu Kα radiation (λ = 1.541838 Å). The 2θ° angle of the diffractometer was tuned from 5 to 80° in steps of 5.000°, with a measuring time of 1.00 minute per step.

Figuer 3.3 Rigaku Multiflex X-RAY diffractometer.

3.3.3 UV-Vis's spectroscopy

The UV-vis absorbance of products was measured using a UV/VIS spectrometer (PerkinElmer). Model: Lambda35 Serial No.: 50251402411 Ultraviolet radiation was used in the range of 200nm to 400 nm.

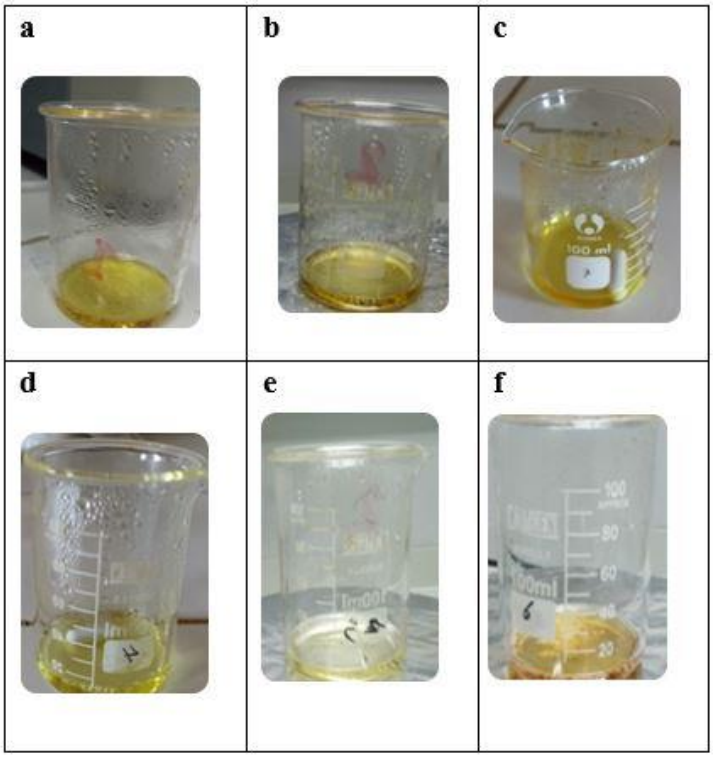
FIguer 3.4 PerkinElmer UV_Vis

4. RESULTS AND DISCUSSION

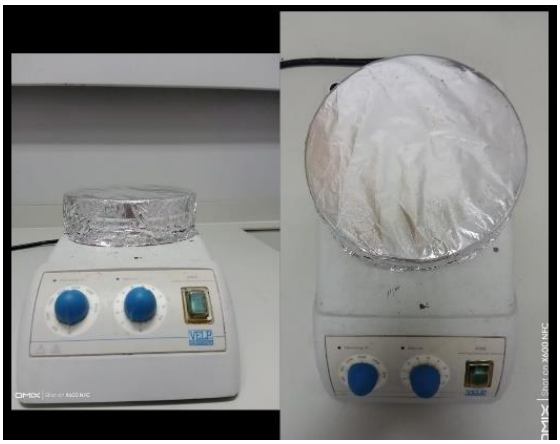
4.1 EXPERIMENTAL PROCESS

4.1.1 Gelation

The minerals $Mg(NO_3)_2$ $6H_2O$, $Zn(NO_3)_2$ $6H_2O$, $Fe(NO_3)_2$ $9H_2O$ and $Al(NO_3)_3.9H_2O$ were dissolved in different molar ratios in 50 ml of distilled water. Then, 0.2M citric acid ($C_6H_8O_7.H_2O$) was added, which was prepared by dissolving 0.2101g in 50 ml of distilled water. The solution was stirred for an 1hour, At a temperature of 80^oC. Next, 2 ml of ethylene glycol ($C_2H_4(OH)$) was added and the mixture was continuously stirred at a temperature of 150 ^oC until it evaporated after no less than 5 hours producing the aimed gel.



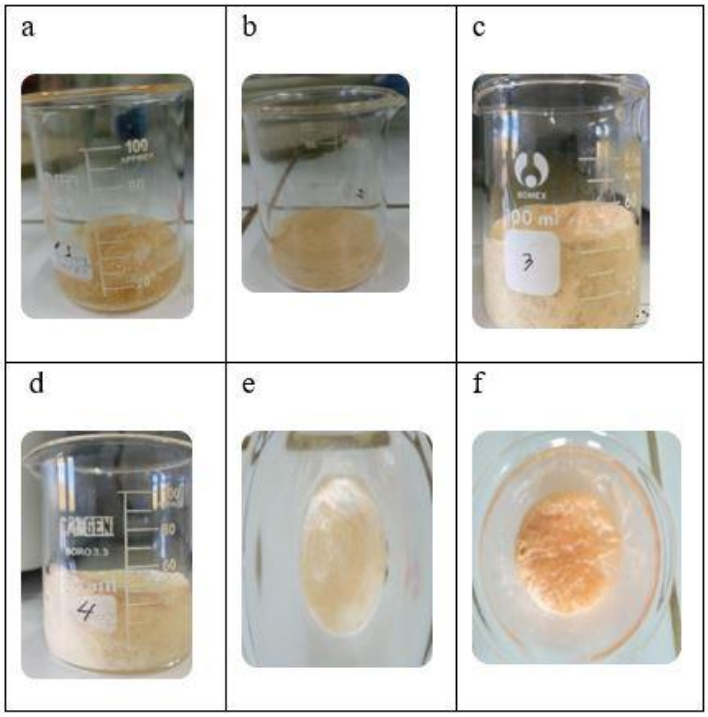
Figuer 4.1 The gelation of a] $MgZn_1Fe_5$\Al b] $MgZn_2Fe_4$\Al c] $MgZn_3Fe_3$\Al d] $MgZn_4Fe_2$\Al e] $MgZn_5Fe_1$\Al f] $MgFe_6$\Al.



Figuer 4.2 Instrunentation Stirring.

4.1.2 Xerogel

After the first step, Xerogel was obtained after putting the gel in the oven for 24 hours at 105 ^{o}C, as shown in the Fig (4.3). The change in xerogel colour was observed because of the different concentrations of Zn and Fe: MgZn0.05Fe0.01Al light yellow colour, MgFe0.06Al dark yellow colour.

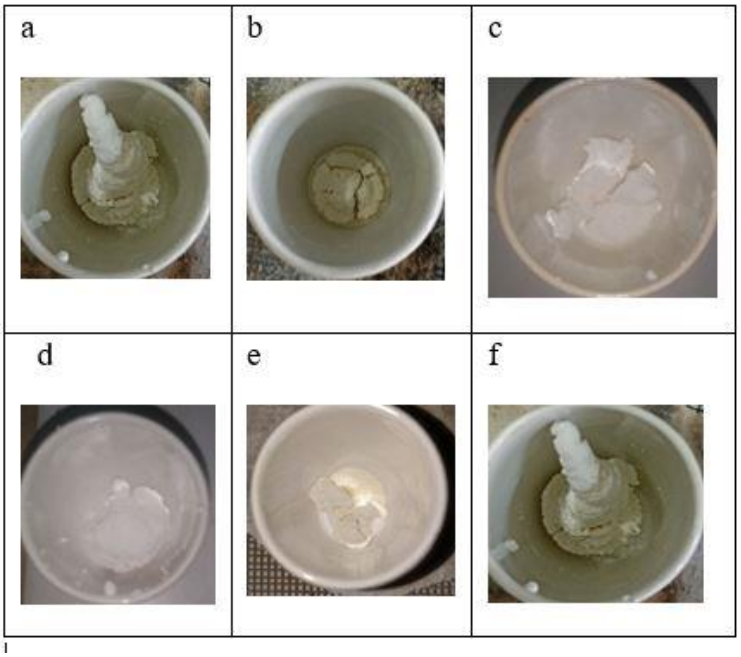


Figuer 4.3 Xerogel of a] $MgZn_1Fe_5$\Al b] $MgZn_2Fe_4$\Al c] $MgZn_3Fe_3$\Al d] $MgZn_4Fe_2$\Al e] $MgZn_5Fe_1$\Al f] $MgFe_6$\Al.

Figuer 4.4 Sterilizer (Oven).

4.1.3 Mixed metal oxides (MMO)

After the Xerogel was ground, it was put in the ash furnace for 4 hours at 650 ^{o}C. The colour change from yellow to white was observed, and mixed metal oxides (MMO) were obtained, as shown in the figure below.

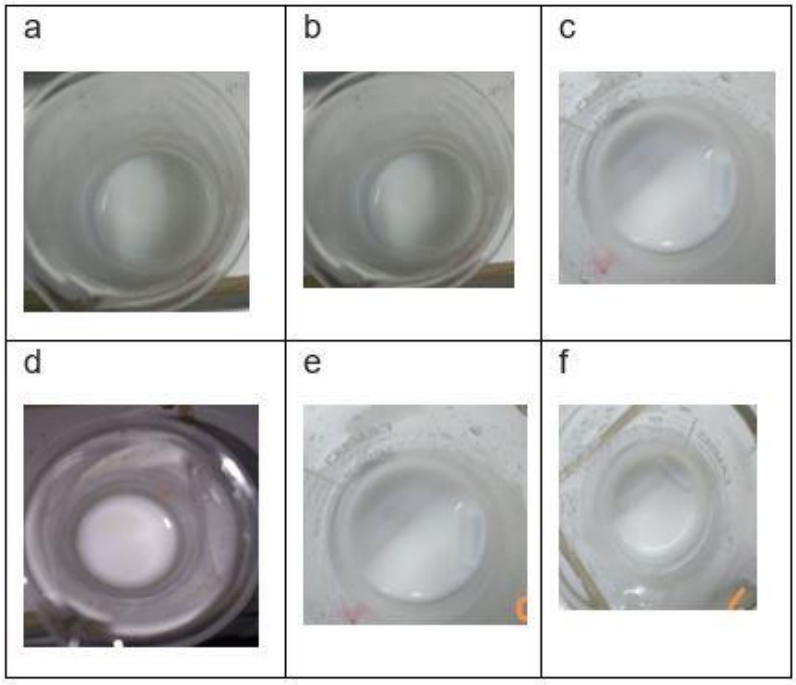


Figuer 4.5 MMO of a] $MgZn_1Fe_5$\Al b] $MgZn_2Fe_4$\Al c] $MgZn_3Fe_3$\Al d] $MgZn_4Fe_2$\Al e] $MgZn_5Fe_1$\Al f] $MgFe_6$\Al.

Figuer 4.6 Ash Furnace.

4.1.4 LDHs

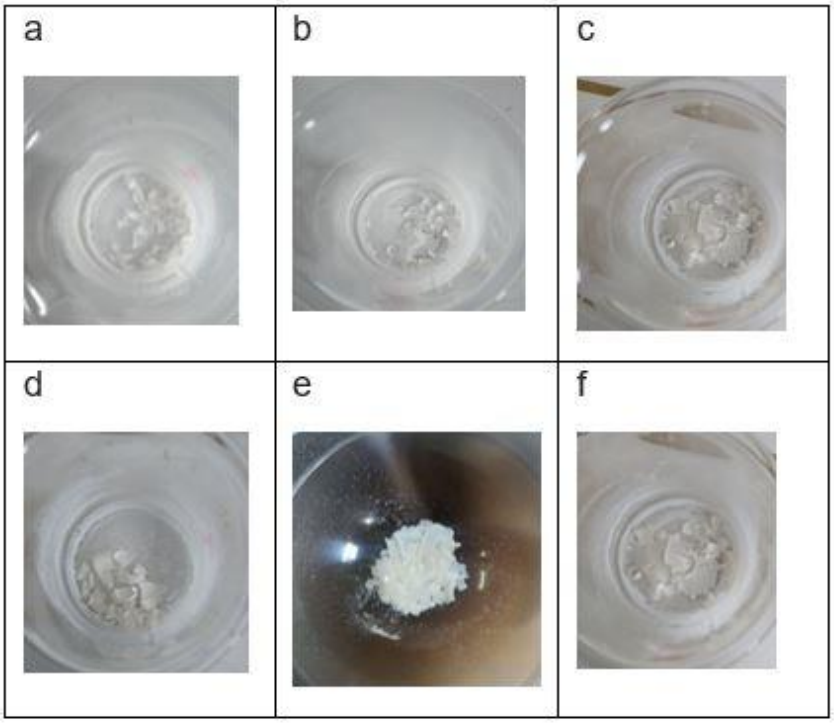
After 6 hours on the stirr at 80 °C, LDH was obtained.



Figuer 4.7 LDH of a] $MgZn_1Fe_5$\Al b] $MgZn_2Fe_4$\Al c] $MgZn_3Fe_3$\Al d] $MgZn_4Fe_2$\Al e] $MgZn_5Fe_1$\Al f] $MgFe_6$\Al.

4.1.5 Reconstruction process of LDHs

Then we was putting in the oven at 12 hr at 70 °C to dry.

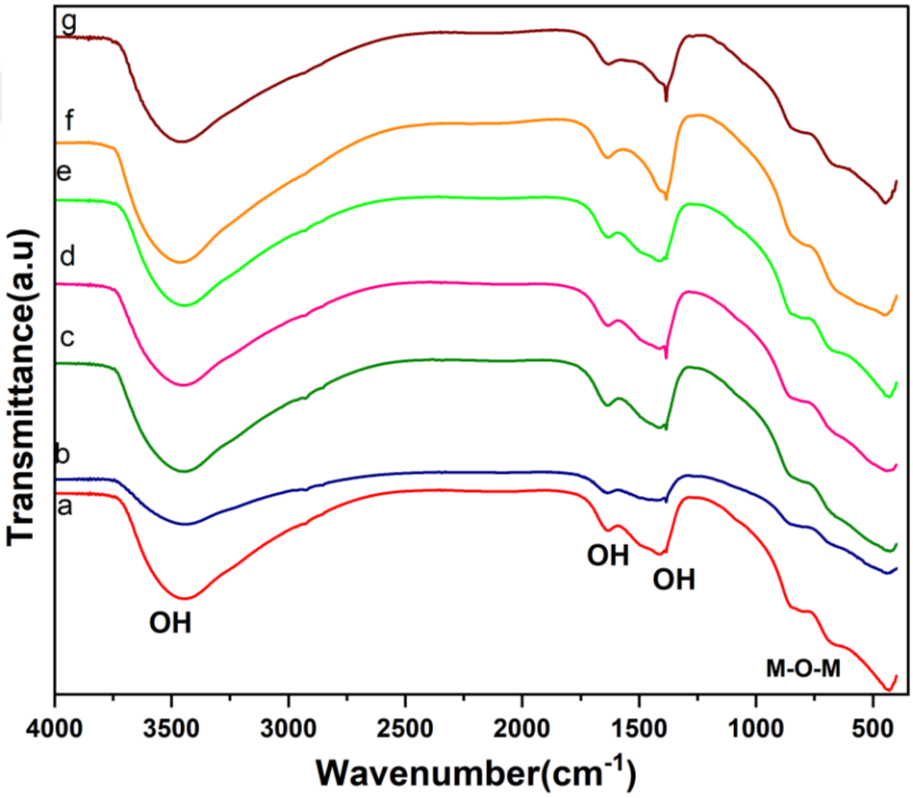


Figuer 4.8 LDH of a] $MgZn_1Fe_5$\Al b] $MgZn_2Fe_4$\Al c] $MgZn_3Fe_3$\Al d] $MgZn_4Fe_2$\Al e] $MgZn_5Fe_1$\Al f] $MgFe_6$\Al.

4.2 Characterization of LDH

4.2.1 FT-IR Spectra of Mixed metal oxied MMO

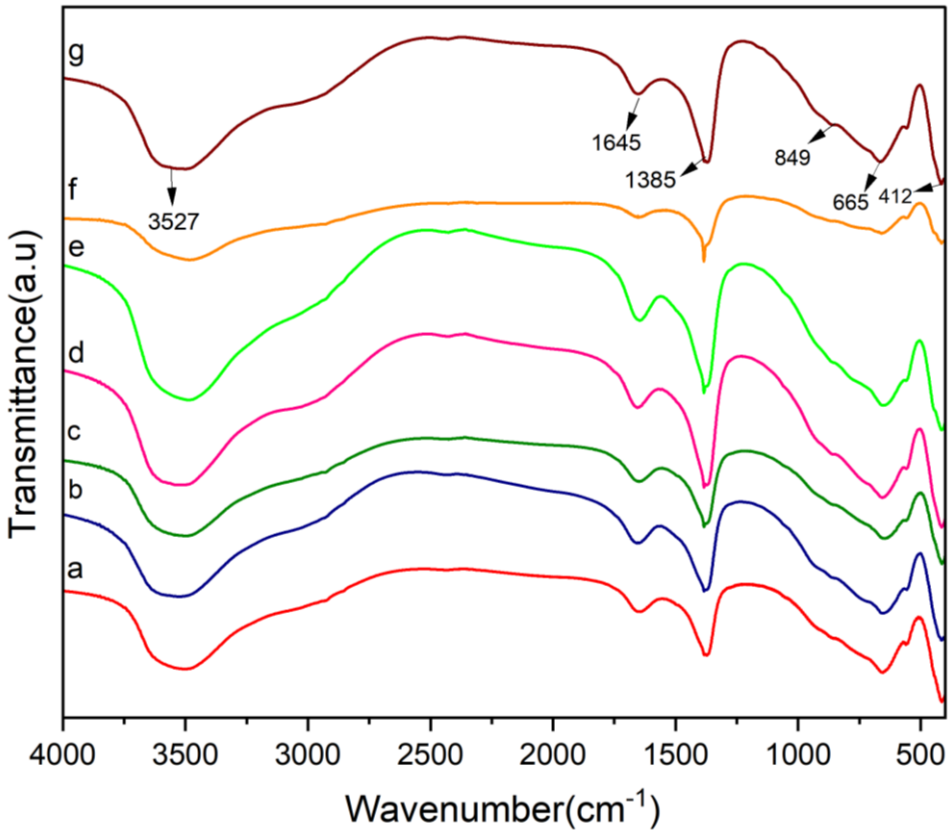
The absorption peaks seen at 3455 cm^{-1} and 1640 cm^{-1} in MMO synthesized at a temperature of 650 C^{o} primarily arise from the O-H stretching vibration of the surface hydroxyl group or the adsorbed water of the M-O-M. The primary peak observed at 1590 cm^{-1} is attributed to the pronounced asymmetric stretching of the C=O bond. The presence of N-O is indicated by the peak observed at 1405 cm^{-1}. The absorption band at 480 cm^{-1} is indicative of the high existence of the terminal oxygen vibration in the M-O-M material(117).



Figuer 4.9 FT-IR Spectra of MMO after 4Hr at 650^{o}C a] $MgZn_1Fe_5$\Al b] $MgZn_2Fe_4$\Al c] $MgZn_3Fe_3$\Al d] $MgZn_4Fe_2$\Al e] $MgZn_5Fe_1$\Al f] $MgZn_6$\Al g) $MgAlFe_6$.

4.2.2 FT-IR Spectra of LDH

The following is the Fourier transform infrared (FTIR) spectrum of Mg-Al (LDH)-NO3, which was synthesized by the sol-gel method employing aluminum and magnesium nitrate. It was found that the band at 3493 cm^{-1} was caused by water molecules and hydroxyl groups in the spaces between the brucite-like layers (118). The presence of H_2O in the interlayer water caused the weak band observed in the 1645 cm^{-1} region. The NO_3^{2-} ions' stretching vibrations ν2, ν3, and ν4 between layers were found to be infrared absorptions at 849, 1385, and 665 cm^{-1} frequencies, in that order. This is what is seen with all hydroxides, no matter what kind of octahedral sheet structure they have (119). It suggests that the anions that are between the layers live in a very balanced environment. The presence of O-M-O bands may account for the spectral peaks observed at 412 cm1 in the low-energy region (120).

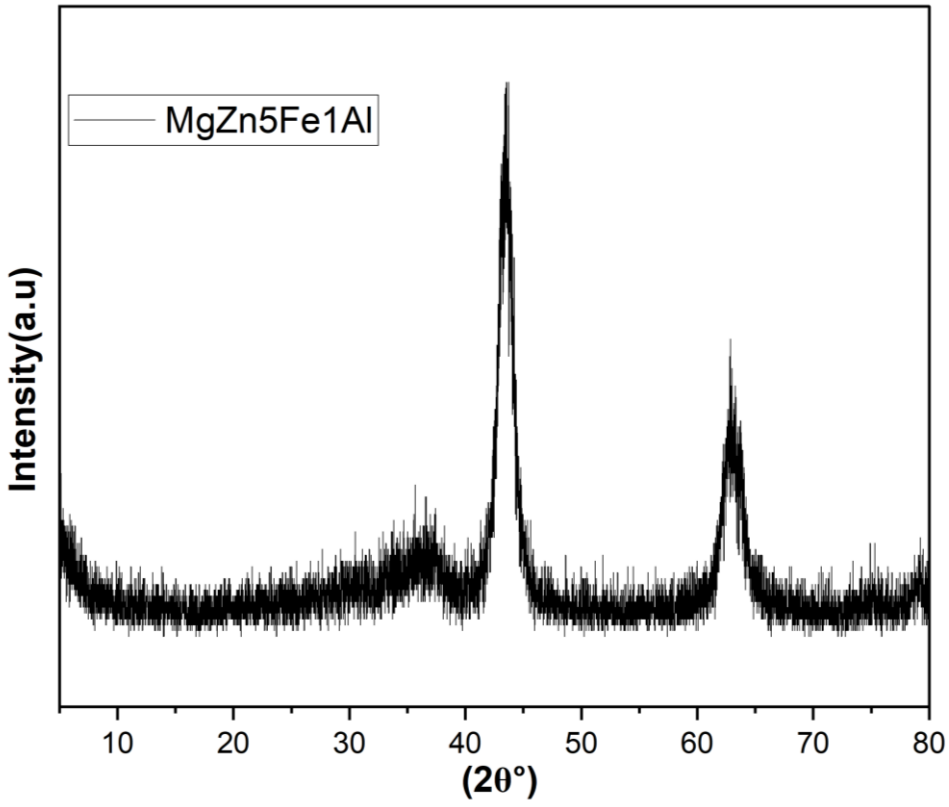


Figuer 4.10 FT-IR Spectra of LDH a] $MgZn_1Fe_5$\Al b] $MgZn_2Fe_4$\Al c] $MgZn_3Fe_3$\Al d] $MgZn_4Fe_2$\Al e] $MgZn_5Fe_1$\Al f] $MgZn_6$\Al g) $MgAlFe_6$.

4.2.3 Analysis XRD of Mixed Metal Oxides (MMO)

In this synthesis method, the synthesised Mg-Al-O (M= Zn/Fe) precursor gels were heated at 650 °C to transform them into mixed metal oxides (MMO). The LDHs were created by building MMO in deionized water at a temperature of 80 °C (105).

We heated the first gels to 650 °C for 4 hours to study the rebuilding properties of layered double hydroxides (LDHs) made with the sol-gel method. Specifically, we looked at those that contained Mg2xMx/Al1 (M = Zn, Fe). Upon heating the sample to a temperature of 650°C, two distinct XRD peaks were observed at 43.49º and 62.88º, suggesting the formation of a mixed metal oxide (MMO) phase with a structure resembling that of MgO.

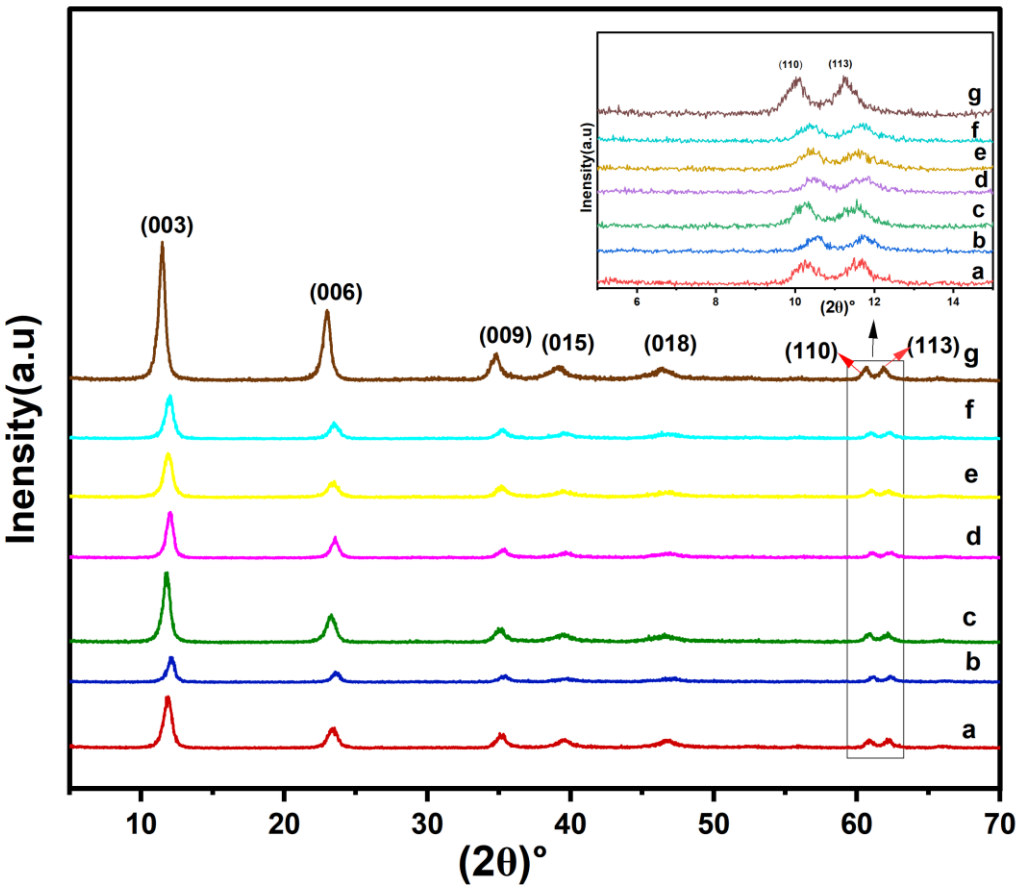


Figuer 4.11 XRD patterns of mixed metal oxides (MMO) obtained by heating the (MgZn5Fe1Al) precursor gels at 650 °C.

4.2.4 XRD of the LDH $Mg_{3-x-y}Zn_xFe_y$\Al1

We used X-ray diffraction (XRD) patterns to look at the phase structure and crystallinity of the samples we made. The sample had a well-formed LDH structure with distinct reflections at angles of 11.98º, 24.34º , 35.73º, 39.60º , 46.83º, 60.99º, and 62.26º. The sharp and powerful peaks observed at low diffraction angles (peaks near 2 = 11.98º, 24.34º, and 35.73º) are a result of diffraction caused by the basal planes (003), (006), and (009). The absence of any detectable peaks corresponding to by-products such as metal oxides or metal hydroxides suggests that the seven LDHs synthesized are of high purity (121).

The diffraction positions of (003), (006), and (009) for all seven LDH samples are identical. The reason for this is that the nitrate ion is present as the interlayer ion in all LDH samples. The presence of wider and less pronounced peaks at larger angles (specifically, peaks near 2 = 39.60º and 46.83º) can be attributed to the diffraction caused by planes (015) and (018), respectively. The two peaks observed at 60–62° can be attributed to the (110) and (113) reflections for LDHs. The variation in the positions of the samples is due to the different sizes of the metal ions (M^{2+}) in the host layer (122). The LDH d-spacing of 7.56 was consistent with a previous measurement conducted by Lee. Based on the findings derived from FT-IR and XRD analyses, it can be concluded that LDHs were successfully synthesised (118).

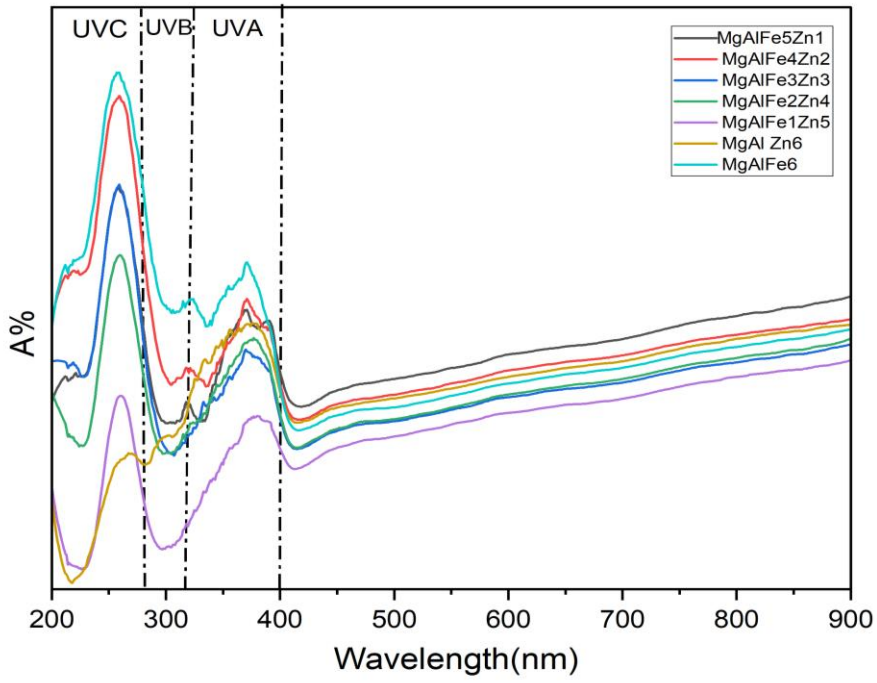


Figuer 4.12 Powder X-ray diffraction pattern of the LDH synthesized a] $MgZn_1Fe_5$\Al b] $MgZn_2Fe_4$\Al c] $MgZn_3Fe_3$\Al d] $MgZn_4Fe_2$\Al e] $MgZn_5Fe_1$\Al f] $MgZn_6$\Al g) $MgAlFe_6$.

4.2.5 UV-VIS reflection Spectra

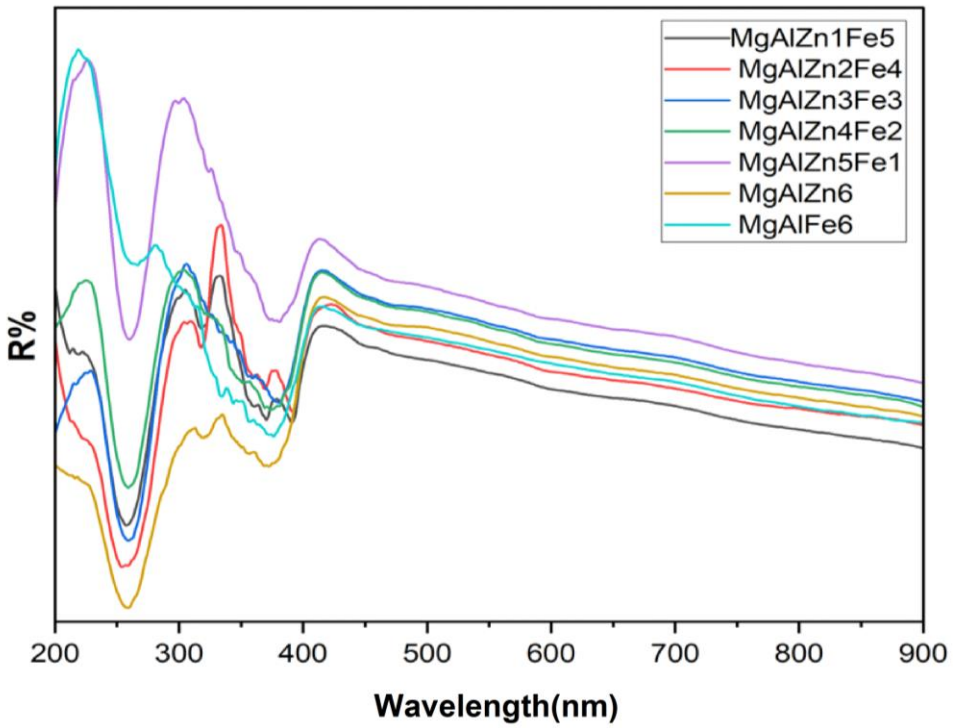
Particles' ability to block ultraviolet light is due to absorption and scattering Because of this, the LDHs' ability to block UV light is mostly determined by how much energy they absorb and how much light they scatter. These factors are related to the samples' natural optical properties and particle size or shape. The way light is scattered is the same for all five LDHs because their shapes and primary and secondary particle sizes are the same. The difference in UV shielding is mostly caused by the way LDHs look on their own (122).

The UV-vis absorption spectra of MII/MgAl-LDHs (M = Mg, Fe, and Zn) were showed in Figure 4.13 to characterize their optical characteristics. Absorbance values of LDH samples were calculated by integrating the absorbance across the wavelength range of 200–400 nm; this revealed that Fe6MgAl-LDHs exhibited higher absorbance values than Zn5Fe1MgAl-LDHs, Zn1Fe5MgAl-LDHs, and Zn2Fe4MgAl-LDHs in the UVB, UVA and UVC areas. Compared to Zn5Fe1MgAl-LDHs, Zn1Fe5MgAl-LDHs, Zn2Fe4MgAl-LDHs, Zn3Fe3MgAl-LDHs, Zn4Fe2MgAl-LDHs, and Zn6MgAl-LDHs, Fe6MgAl-LDHs have higher absorbance values(122).



Figuer 4.13 UV-VIS reflection Spectra of MgZnFe/Al LDH.

Absorption is the amount of light absorbed by the sample during the measurement and R is the amount of light reflected. So, A is the opposite of R and vise versa.



Figuer 4.14 UV-VIS reflection Spectra of MgZnFe/Al LDH.

5. CONCLUSIONS AND RECOMMENDATIONS

The primary findings of the study can be succinctly summarised as follows:

1- The Mg3-xMx/Al1 (M =Fe, Zn/Mg Al) layered double hydroxides (LDHs) were effectively synthesized utilizing an aqueous sol-gel method. The process included the transformation of mixed metal oxides into layered double hydroxides using either water or a solution of magnesium nitrate.

2- The precursor gels were broken down at 650^{o}C, and then the crystalline MMO powders were dried and then rehydrated in water to make the LDHs using this watery sol-gel manufacturing technique.

3- The sol-gel technique proves to be successful in producing LDHs and is suitable for studying substitution effects in various multinary metal systems. Moreover, this synthesis pathway is cost-efficient.

4- Upon subjecting Mg-Al-O precursor gels to a temperature of 650°C, the X-ray diffraction (XRD) analysis of the resultant mixed metal oxide (MMO) sample showed the existence of a single phase of MMO. Results showed that the microstructure of (MMO) created by rebuilding sol-gel-generated layered double hydroxides (LDHs) displayed a characteristic known as the "memory effect." This impact suggests that the MMO has many of the same microstructural properties as the LDHs.

5- MgZnAl and MgZnFeAl, MgFeAl layered double hydroxides (LDHs) were effectively synthesized in this study using the sol-gel process and a 3.1 molar ratio. FT-IR spec-trophotometer studies and X-Ray Diffractograms have been used to describe the outcome. In comparison to MgZnFe/Al LDHs (9.57 Å) and MgAl/Fe (8.66 Å), inter-layer MgZnAl was found to have the highest value (10.15 Å) in the XRD data. Therefore, a synthesis of layered double hydroxides and their characterization may be provided in this work.

6- The UV-shielding performance of layered double hydroxides (LDHs) is significantly affected by both particle size and composition, and these factors will mutually influence each other. In this work. The UV–vis spectra show that the Fe6MgAl-LDHs exhibit the highest absorbance than Zn5Fe1MgAl-LDHs, Zn1Fe5MgAl-LDHs, and Zn2Fe4MgAl-LDHs in the UVB and UVA and UVC areas. Compared to Zn5Fe1MgAl-LDHs, Zn1Fe5MgAl-LDHs, Zn2Fe4MgAl-LDHs, Zn3Fe3MgAl-LDHs, Zn4Fe2MgAl-LDHs, and Zn6MgAl-LDHs, Fe6MgAl-LDHs have higher and this result is in good accordance with the UV-shielding performance,

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