

Introduction

1.1 Purpose of the study

Harnessing a clean, affordable, and inexhaustible energy source, its storage, and addressing environmental pollution necessitates extensive scientific attention. Currently, the environment pays the price of excessive fossil fuel consumption with a massive 31.5 GT of carbon emission, which can be curbed by switching to green energy technologies. (IEA, 2020) Scholars are interested in alternative energy because of the loss of these finite resources and their negative environmental effects. The supply of renewable energy is widely available from nature. The demand for alternative energy technologies will rise in the future as our thirst for green energy grows. The fluctuation of seasonal changes encourages the storage of renewable energy in hydrogen, a fuel made from biomass, for use at a later time. Renewable energy from solar and wind sources is diffuse and irregular in nature. A greener, more attractive solution to this problem would be catalytic hydrocracking to produce biofuels and an electrocatalytic process to produce Hydrogen fuel. Hydrogen is high-energy-density, pollution-free fuel and can be easily stored and transportable. Hydrogen can use directly as fuel and also can consumed indirectly in a hydrogen fuel cell, produce only water as by-product. Additionally, the Fischer-Tropsch, organic hydrogenation and ammonia synthesis use hydrogen as a crucial feedstock. Hydrogen fuel from electrocatalytic water splitting provides an alternative greener fuel option owing to its zero-emission by-products to fulfils the worldwide energy consumption.(Yamada et al., 2016, Yang et al., 2020)

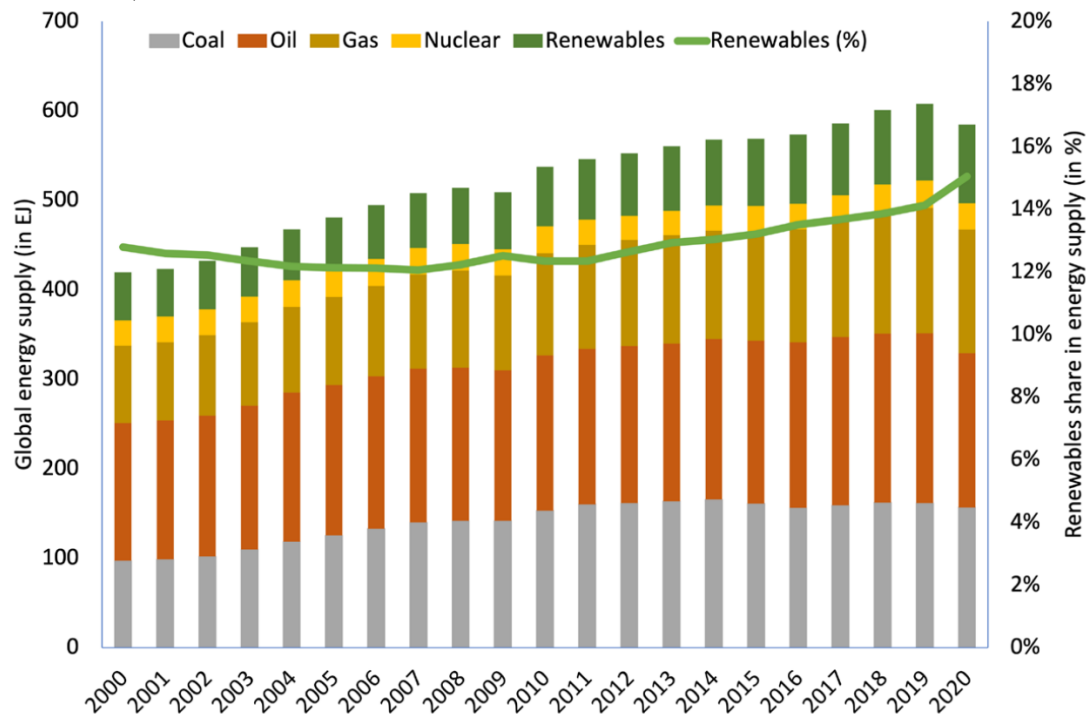


Figure 1.1: Total primary energy supply globally (Source: GLOBAL BIOENERGY STATISTICS 2022, WBA).

Currently, Fossil fuels provide the largest portion of the world's energy. The total primary energy supply was 585 EJ in 2020, with fossil fuels accounting for 80% of the total (Coal 27 percent, Oil 29 percent and Gas 24 percent) Nuclear power's TPES was 29,2 EJ, making up 5% of the total energy mix as shown in Figure 1.1. Solar, wind, water, biomass, geothermal, and other renewable energy technologies made up 15% of the primary energy supply in 2020, an increase of 0.9% from the previous year. Biomass is one type of renewable energy source that may be converted into biofuels, which have several benefits over fossil fuels in order of reducing greenhouse gas

emissions, boosting energy independence, and enhancing the livelihood of farmers. The liquid, gas, or solid fuel produced from a renewable biomass feedstock, is referred to as a biofuel. Examples of biofuels include biodiesel, bio jet-fuel, biomethanol, biohydrogen, biosynthetic gas, bioethanol, biomethanol, biomethane, as well as liquids created via Fischer-Tropsch technology (Liuzzi et al., 2022, Krishna et al., 2023). Since agricultural products make up a large portion of the feedstock used to produce biofuels, they act as a link between the farming and energy industries. Crop leftovers as a possible source of feedstock for bioenergy production have recently attracted considerable attention since they are not in a position to undermine efforts to provide food for human use. Around the world, the transport sector used 4,23 EJ of renewable energy in 2020, with liquid and gaseous biofuels making up 90% of all the renewable energy used in the industry. The percentage of renewable power (estimated based on the share of renewables in the entire electrical industry) was 10%.

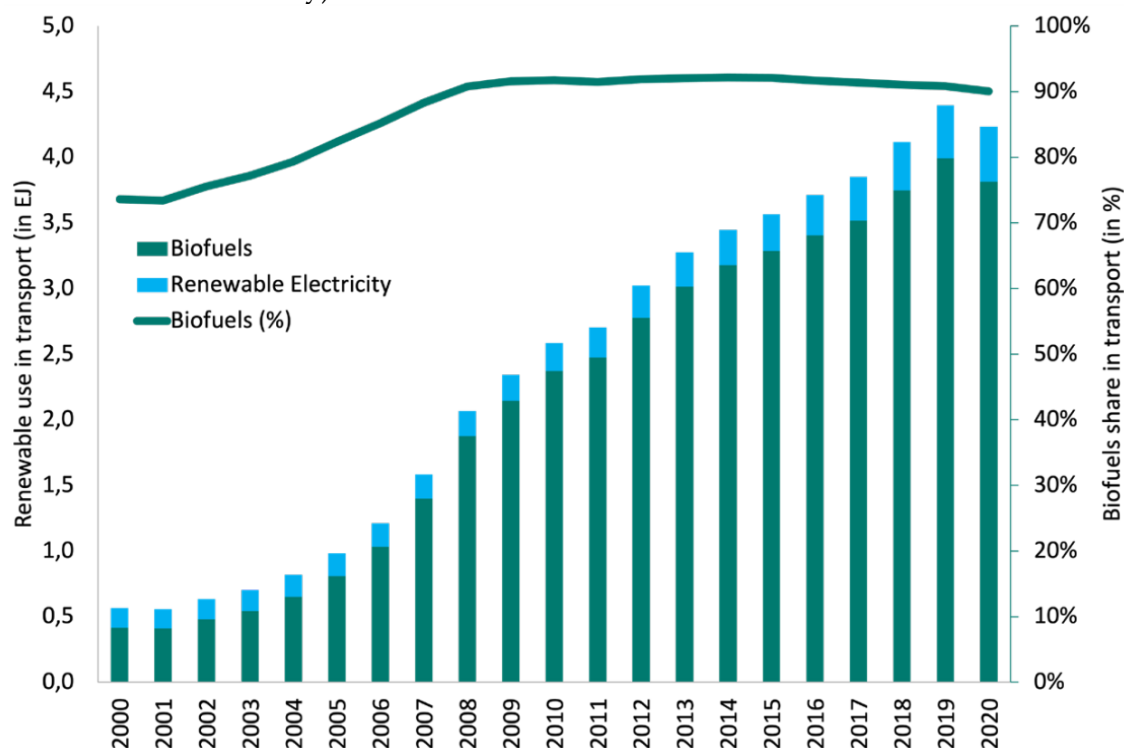


Figure 1.2: Renewable energy use in transport globally (Source: GLOBAL BIOENERGY STATISTICS 2022, WBA).

Biofuels are fuels produced from biological processes. Primary biofuels typically consist of fuelwood, wood chips, and organic materials and are used to prepare food and generate heat or electricity as shown in **Figure 1.2** (Olguin-Maciel et al., 2020). Secondary biofuels are derived from agricultural crops, and forestry waste biomass. Over the past five decades, non-food feedstock sources for secondary biofuel production have been explored and utilized in transportation. First-, second-, third-, and fourth-generation biofuels are the four categories into which biofuels are split based on the biomass feedstock.

Another major issue is the rising contamination of water resources brought on by reckless human behaviour, such as the deliberate dumping of industrial pollutants into freshwater sources. The millions of contaminated waters destroy the ecosystem of oceans, rivers, lakes and ponds. Aquatic life is becoming deadly as a result of the widespread use of colours in the textile and paper industries. As a potential solution to many environmental problems, electrocatalysis and photocatalytic degradation of pollutants (Dyes, antibiotics, and heavy metals) using nanomaterials are profuse scientific interests to positively impact human health and the environment (Chen et al., 2020a). Therefore, efforts have been concentrated on discovering suitable treatment methods to take these toxins out of wastewater. Adsorption, filtration coagulation, Fenton oxidation, biological, photocatalytic and electrocatalytic treatment methods are just a few of the strategies that have been researched for the removal of toxic dyes (Valli Nachiyar et al., 2023). The utilization of cheap, readily available, and visible-light-driven

photocatalysts has gained attention in the photocatalysis community as a way to efficiently use solar energy (Valli Nachiyar et al., 2023).

Magnetic measurements can investigate the magnetic structure and electrical properties of active magnetic catalyst utilized in lithium-ion battery technology. Li-ions have a nonmagnetic (diamagnetic) nature, indirectly affecting magnetic characteristics by influencing the cation valence of other lattice elements. The type of metal ions and electronic states determine the magnetic characteristics of the sublattice in the oxide framework. The magnetic properties can easily identify the minor variations that SEM, TEM, FITR, and XRD cannot detect. Therefore, magnetism is also one of the essential tools for material properties, which easily checks the quality of the materials. Apart from the energy storage applications, the Li-Mn-O family has piqued interest in magnetic interaction due to its orbital orientation changes at very low temperatures.

1.2 Objectives and scope

The key aim of this thesis is to develop efficient nanomaterials, that can act as a good support and as well as catalyst with tuneable physiochemical properties. In this thesis work, we have synthesised the ZnO doped MXene, Iron doped $\text{SiO}_2\text{-Al}_2\text{O}_3$ and Gd doped LMO for various applications relating to electrocatalytic HER, photocatalytic pollutant degradation and energy storage. One of the limiting factors to find a highly effective materials with excellent bandgap alignment that absorb the major portion of solar spectra. The study undertaken in this thesis attempts to address some of these issues. The main objectives for the thesis work are listed below:

1. The study aims to investigate novel nanomaterials with improved properties using one-pot synthesis.
2. To study and analyse the properties of the synthesized materials using various characterization techniques.
3. To investigate the synergistic impact of Ti_3C_2 and ZnO for photocatalysis and electrocatalysis applications, a straightforward hydrothermal synthesis of ZnO- Ti_3C_2 MXene nanocomposites with varied weight percent of ZnO.
4. $\text{Ti}_3\text{C}_2\text{T}_x$ and ZnO- $\text{Ti}_3\text{C}_2\text{T}_x$ catalysts were synthesized and demonstrated for selective hydrodeoxygenation reaction (HDO) of methyl oleate (MO) as the model compound for producing liquid fuels and value-added chemicals with significantly low CO_2 footprints.
5. This study also aims to focus on solvent-free bio-jet fuel generation (C8 to C15) from model substrate methyl oleate using variable iron-loaded $\text{SiO}_2\text{-Al}_2\text{O}_3$ solid acid catalysts.
6. This work includes a section on the exploration of a range of Gd^{3+} doped LiMn_2O_4 synthesis utilising a straightforward one-step sol-gel synthesis as well as a systematic analysis of the impact of increasing Gd^{3+} concentration on magnetic characteristics.

1.3 Brief results and future perspective of the work

A variety of materials synthesis $\text{Ti}_3\text{C}_2\text{T}_x$, ZnO- $\text{Ti}_3\text{C}_2\text{T}_x$, Fe- $\text{SiO}_2/\text{Al}_2\text{O}_3$ and Gd- LiMn_2O_4 characterization, and applications have been used to carry out numerous pertinent experiments to accomplish the goals outlined in the study presented in this thesis. The study has great promise for the electrocatalytic HER, photocatalytic dye degradation and biofuel production applications. The materials have also been explored for magnetic application with a correlation with Raman and DFT. The study also offers an efficient route for converting edible and non-edible vegetable oils to biofuels.

Role of ZnO in ZnO Nanoflake/ Ti_3C_2 MXene Composites in Photocatalytic and Electrocatalytic Hydrogen Evolution (chapter 3: ACS Appl. Nano Mater. 2022, 5, 7, 9319–9333)

The study in this chapter was undertaken to understand and synthesize nanomaterials that can be useful for electrocatalytic HER and photocatalytic organic pollutant degradation. Herein, we report a synergistic impact of Ti_3C_2 and ZnO for photocatalysis and electrocatalysis applications, a straightforward hydrothermal synthesis of ZnO- Ti_3C_2 MXene nanocomposites with varied weight percent of ZnO (**Figure 1.3**). The effectiveness of ZnO- Ti_3C_2 nanocomposites in degrading organic contaminants (such as dyes and pharmaceuticals drugs) and in the

hydrogen evolution process (HER) has been thoroughly studied. Among the developed nanohybrid catalysts, ZnO-Ti₃C₂ composite with 10 wt.% ZnO (MXZnO-10) showed the highest photodegradation efficiency of 76.4% within 10 minutes of the reaction and 99.2% in 60 minutes for methylene blue (MB) dye. The longer lifetimes of electrons and holes were made possible by the synergistic interactions between 2D layered Ti₃C₂ and ZnO, which decreased the recombination rate. The MB dye was more efficiently degraded attributed to the uncombined electrons and holes. Excellent HER performance was demonstrated by the 5 wt % ZnO-Ti₃C₂ (MXZnO-5) nanocomposite with overpotential of 495 mV at 10 mA/cm² and a Tafel slope of 108 mV/dec. This work widens the application range of transition metal oxide-MXene composites, providing potential substitute materials for photocatalysis and electrocatalysis applications.

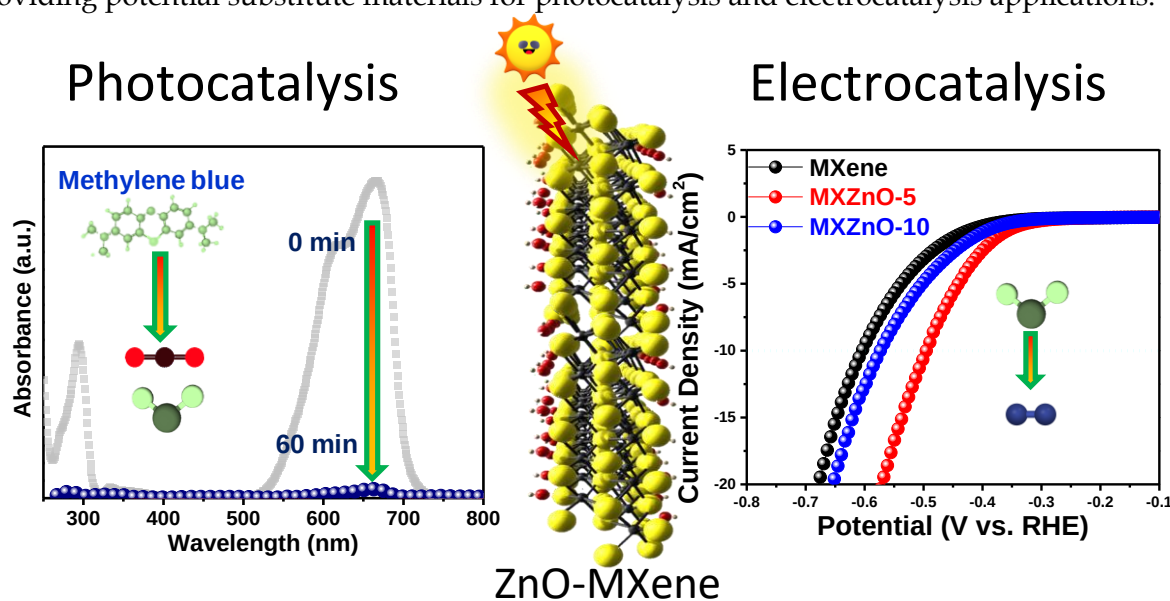


Figure 1.3: Electrocatalytic Hydrogen evolution reaction and Photocatalytic degradation of industrial dyes using the synthesized ZnO-Ti₃C₂.

On the reduction of CO₂ footprint via selective hydrodeoxygenation by ZnO-Ti₃C₂T_x catalyst under solvent-free conditions (chapter 4: RSC Green Chem., 2023,25, 5470-5482)

This chapter addresses one of the major issues of biofuel production from biomass feedstock by developing a good metal oxide-support material for catalytic HDO reactions (**Figure 1.4**). Biomass-derived fatty acids are essential feedstock for producing liquid fuels and value-added chemicals with significantly low CO₂ footprints. Herein, Ti₃C₂T_x and ZnO-Ti₃C₂T_x catalysts were synthesized and demonstrated for selective hydrodeoxygenation reaction (HDO) of methyl oleate (MO) as the model compound. The synthesized ZnO-Ti₃C₂T_x catalyst showed 100% conversion of MO with >90% selectivity for HDO product (n-C18). Additionally, the pure Ti₃C₂T_x demonstrated 100% conversion with a selectivity of 67% for n-C17 hydrocarbon via the decarboxylation route. The highest reduction of CO₂ footprint is achieved at 280°C and 30 bar H₂ pressure under solvent-free conditions using ZnO-Ti₃C₂T_x. The catalyst is recyclable and reusable after five test cycles. The high catalytic selectivity of the ZnO-Ti₃C₂T_x catalyst towards HDO is attributed to the synergic effect of Ti and ZnO active sites with a robust and thermally stable structure. The study offers an efficient route for converting edible and non-edible vegetable oils to biofuels by controlling CO₂ production.

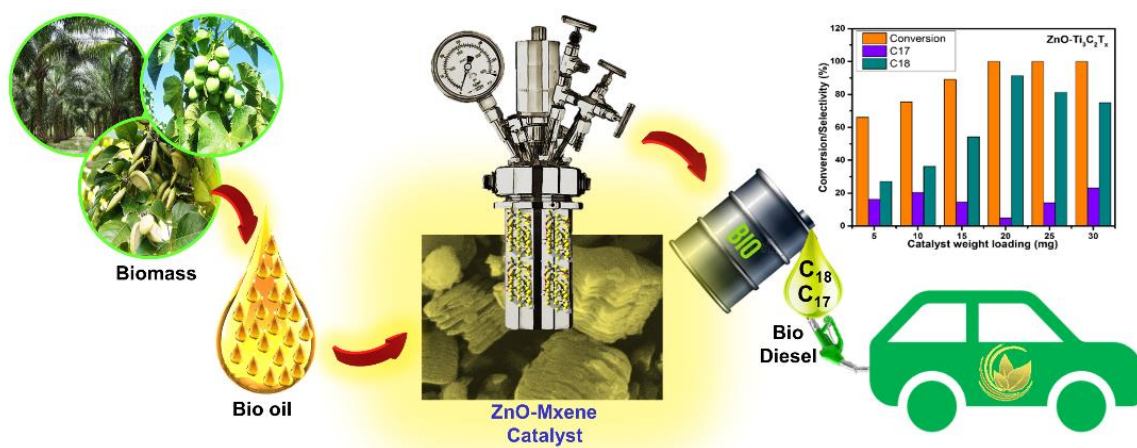


Figure 1.4: Biodiesel production from biomass feedstock using $Ti_3C_2T_x$ and $ZnO-Ti_3C_2T_x$ catalysts.

Highly selective production of bio-jet fuel grade alkanes over an $Fe/SiO_2-Al_2O_3$ solid acid catalyst under solvent-free conditions (Chapter:5: RSC sustainable Energy & Fuels, 2023, 7, 2568-2581)

In this chapter, we are proposing earth-abundant, low toxic and thermally stable Fe-loaded $SiO_2-Al_2O_3$ as a suitable catalyst for highly selective Bio-jet fuel production (**Figure 1.5**). In this chapter, an effective sulphur-free and non-noble catalyst (Fe-doped $SiO_2-Al_2O_3$) has been developed with highly dispersed, excellent acidic sites and high surface area to obtain remarkable selectivity and reusability. Catalytic hydrotreatment of methyl oleate over Fe-loaded $SiO_2-Al_2O_3$ catalysts was successfully achieved with complete conversion at 380°C, 5 bar, and 5 h. It has been found that the amount of Fe and acidity of $Fe-SiO_2-Al_2O_3$ significantly impacted the product distribution and conversion to hydrocarbons. The temperature effects revealed that high temperature (380°C) conditions are suitable for bio jet fuel and lower temperature range (300 and 320°C) is suitable for the bio-diesel range. The maximum conversion and selectivity were obtained for 10 wt.% Fe-doped $SiO_2-Al_2O_3$ catalyst is 100% and 74.13%, respectively. The catalyst maintains excellent reusability up to 10 cycles towards bio-jet fuel. In summary, the results were very promising, especially considering the high acidity and unique textural properties of the catalyst at relatively mild process conditions as low H_2 pressure in solvent-free conditions.

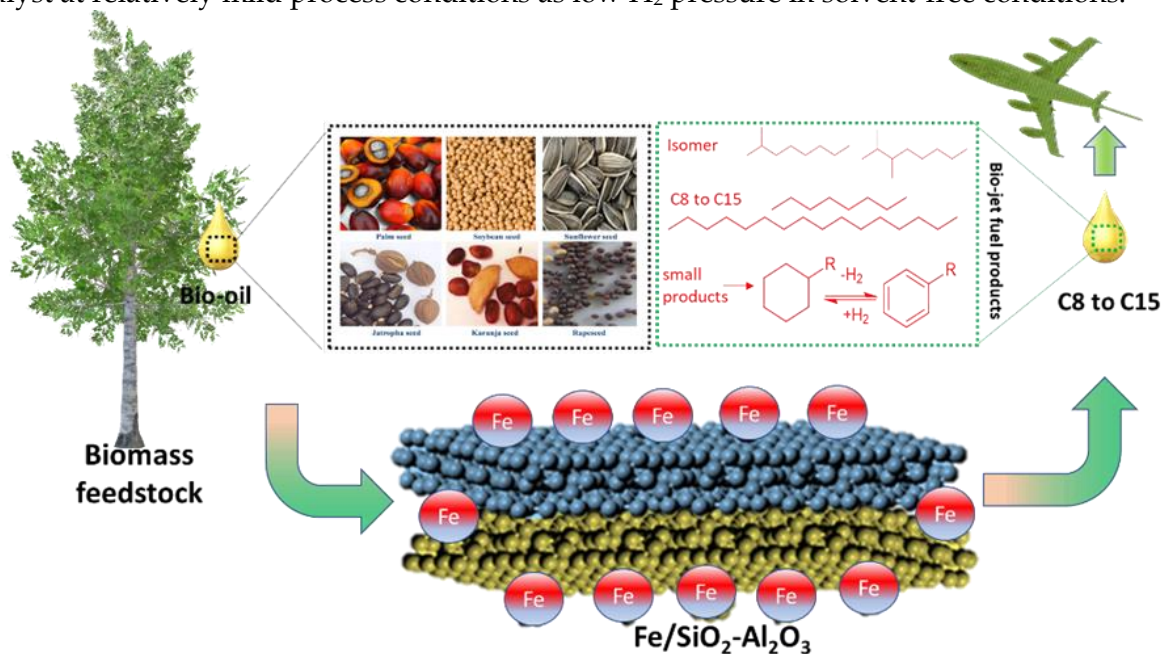


Figure 1.5: The earth-abundant, low toxic and thermally stable Fe-loaded $SiO_2-Al_2O_3$ as a suitable catalyst for highly selective Bio-jet fuel production.

Impact of Gadolinium Doping into the Frustrated Antiferromagnetic Lithium Manganese Oxide Spinel. (Chapter 6: *iScience*. 2023 Jan 20;26(1):105869)

The main objective of the work carried out in this chapter is to correlate the energy storage properties ($\text{Gd-LiMn}_2\text{O}_4$) with magnetic properties (**Figure 1.6**). This section is about the extensive electrochemical characteristics, cubic spinel LiMn_2O_4 (LMO) is a promising electrode material for cutting-edge technological gadgets. Here, a series of Gd^{3+} doped LiMn_2O_4 were synthesized using a straightforward one-step sol-gel synthesis. This allowed for a systematic investigation of the impact of increasing Gd^{3+} concentration on magnetic characteristics. The magnetic characteristics of the produced materials were associated with the Raman and DFT computations; it was found that the doped LMO had a higher coercivity value than pristine LMO, which scaled down from 0.57T to 0.14T with an increase in Gd concentration. As a result of the Mn^{+2} or Mn^{+3} ions being replaced by Gd^{+3} ions from the octahedral 16d lattice location, the samples displayed a paramagnetic (at 300K) to antiferromagnetic (at 5K) transition and fluctuation in the magnetic moment. The superexchange process is revealed to be responsible for the phase changes that were detected in the hysteresis curve below the Neel temperature (T_N) at 5K.

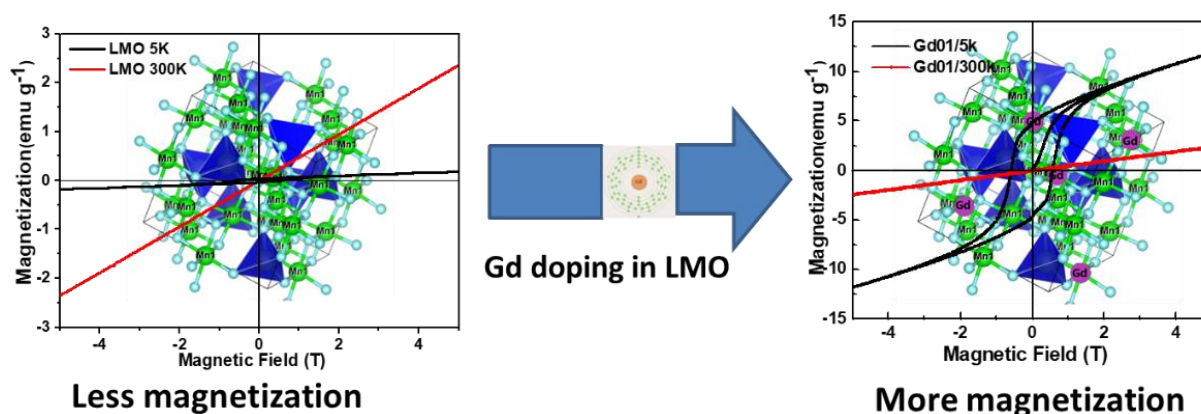


Figure 1.6: Effect of magnetization after Gd doping in LMO.