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By

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Solvothermal synthesis and caraterisation of doped ZnO nanoparticules

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Dedication

This dissertation is dedicated to

my beloved parents

My beloved sisters "Khawla", "Saadia" and "Fatima".

My brother "Zakaria"

Without forgetting my dear comrades on the path of seeking knowledge, "Warda" "Menal" "Loubna achwaq".

All my friends and those close to my heart

And all my teachers

whose unconditional love, support and patience were vital in the completion of this work.

All love

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Introduction

Nanotechnology is an interdisciplinary field with enormous potential in the fields of clean energy, medicine, astronomy, chemistry, physics, agriculture, nano-electronics, and environmental remediation. It integrates the basic principles of engineering with different areas of science, with results that are becoming indispensable for human life.

Nanoparticles are the particles at the subatomic level and possess size-dependent properties(within size range of 1–100 nm), when particle's size becomes nanoscale, their physical, chemical, biological, catalytic, and optical properties become drastically different from their bulk counterparts. Scientists are able to create new systems, multifunctional materials, and nanodevices by exploiting the novel phenomenona of nanomaterials, such as quantum size effect and their large surface to volume ratio, and thus, controlling matter at the atomic, molecular, and supramolecular levels [1]]
In the last twenty years, the attention of researchers is on metal oxide nanoparticles (metal acts as ction and oxygen act as an anion.) as they show a significant difference in its unique electronic, optical, mechanical, magnetic and chemical properties. One of materials that has been in great interest from wide range of technological field associated with nanotechnology is zinc oxide (ZnO) [2]. Due to its wide band gap (3.3 eV) and large exciton binding energy (60 meV), Zinc Oxide (ZnO) has drawn a lot of attention for nanoscale electronic and optoelectronic device applications [3] .
It is used in many applications, such as catalyst, gas sensor, filtering materials for ultraviolet light, and also antimicrobial material. The physical and chemical properties of ZnO nanocrystals can be efficiently tailored by doping of suitable element into the host matrix for a wider range of possible applications. Researchers paid tremendous attention to doping of wide range of elements (Ni, Fe, Mn, Ag, Cu, Cd, Al, La, Ce

etc.) in ZnO [4] [5] [6] . The selection of dopant element is aimed to improve the properties of ZnO nanostructures for a particular practical application. ZnO nanoparticles, doped with transition metals (Ni, Fe, Co etc.) and rare-earth metals (La, Ce, Nd etc.), present enhanced ferromagnetic behavior at room temperature and gained more interest for fabrication of spintronic devices. The improved luminescence property of ZnO nanomaterials, doped with alkali metals (Li, K, Na etc.) enables them for phosphor applications [25]. Doping of ZnO nanocrystals with suitable transition metals, rare metals and noble metals has been preferred to modify their optical and electrical properties, ensuring promising applications of ZnO nanostructures for optoelectronic devices [26, 27]. These properties can be further enhanced by varying stoichiometric ratio of dopant element in host material . [9]
Among the different metallic doping elements Cu.
Cu shows properties as luminescent activator and as compensator for n-type semiconductors, ZnO is known to improve dispersion of copper and its reducibility. Cu functions as a catalyst in ZnO nanoparticle growth if incorporated as a dopant during synthesis, Cu– ZnO enhances antirust property [17]. Cu behaves as an acceptor in ZnO with its energy level locating at 0.17 eV below the bottom of the conduction band, So Cu is important because :
(i) it is a prominent luminescence activator, which can modify the luminescence of ZnO crystals by creating localized impurity levels, (ii) it has many physical and chemical properties that are similar to those of Zn, and (iii) It can change the microstructure and the optical properties of the ZnO system.
There are different physical or chemical synthesis methods have been used to prepare the ZnO nanoparticles such as thermal decomposition [10], thermolysis , chemical vapour deposition, sol–gel [11] , spray pyrolysis [12], precipitation [13] , vapour phase oxidation , thermal vapour transport, condensation, co-precipitation and Solvo/hydro thermal [14]; such a presentation will be only focussed on the potentialities of solvothermal reactions in materials synthesis.

Solvothermal reactions have been mainly used to preparing micro- or nanoparticles with different morphologies, This technique is based on thermal decomposition of organometallic compound in organic solvent and has been successfully applied for the synthesis of various types of nanosized metal oxide with large surface area, high crystallinity and high thermal stability [15]. Solvothermal reactions are mainly characterized by different chemical parameters (nature of the reagents and of the solvent)

and thermodynamical parameters (in particular temperature, pressure) [16].

This work is consists of three chapters, a general introduction and a general conclusion.

The first chapter is devoted to the presentation of a bibliographical summary on nanoscience, nanotechnology and nanomaterials, zinc oxide (ZnO) and its physico-chemical properties.

The second chapter is also organized in two parts, the first part is a description of the ZnO nanopowder production method.

In the second part of this chapter, we present the principle of the experimental techniques of characterization of the nanopowder produced, namely X-ray diffraction, FTIR spectroscopy, analysis thermogravimetric.

The results obtained concerning the physicochemical properties of nanopowders of ZnO / Cu-doped ZnO are exposed and discussed in the third chapter.

Chapitre 1

Zinc Oxide nanostructure: Properties and applications

This chapter is devoted to generalities on nanoscience ,nanotechnology and nanomaterials and the general properties of the material zinc oxide (ZnO). We will talk about its crystallographic structure, its optical properties and its Luminescence properties. At the end of the chapter, we summarize some of present and future applications of zinc Oxide.

1.1 Nanoscience and Nanotechnology

Nanoscience is the science of objects with typical sizes of 1-100 nm. If matter is divided into such small objects the mechanical, electric, optical, and magnetic properties can change. Interfaces rather then bulk properties dominate. Quantum effects due to the size limitation come into play. Nanoscience and Nanotechnology are interdisciplinary, crossing boundaries between physics, chemistry, chemical, electric and mechanical engineering. [18] .
The prefix 'nano'is mean one-billionth (10-9) part that coming from Greek was used in order to describe something really small, as shown in figure 1.1. Therefore, nanoscale is comprehended, with at least one spatial dimension, between 1 and 100 nm.
Both areas, nanoscience and nanotechnology, were emerged with Richard Feynman's conference growing together since 1959.
Nanoscience is the study of nanoscale materials employing the nanotechnology to characterize their specific physical, chemical and biological behaviours due to the influence

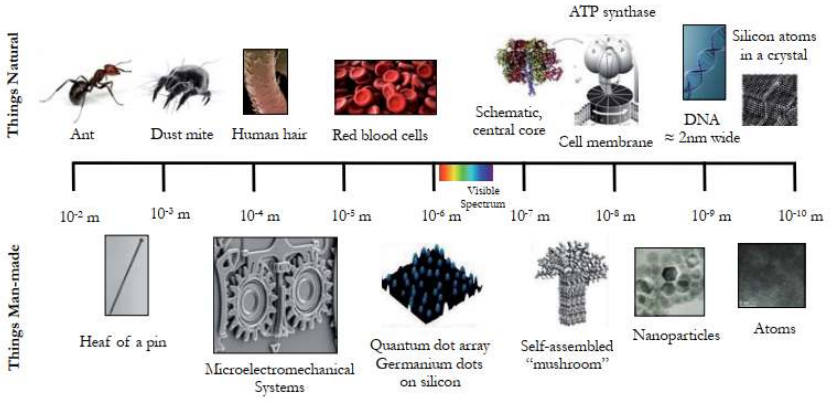

FIGURE 1.1 – Size scale of nanoscience and nanotechnology

of their small dimensions.

Nanotechnology is the technology of design, fabrication, manipulation, and applications of small structures (nanostructures) or small-sized materials (nanomaterials). [19]

1.2 Nanomaterials

There are many definitions of the term "nanomaterial". The European Commission proposed in October 2011, as part of a recommendation1, a definition for the term "nanomaterial". A nanomaterial is a natural material, accidentally formed or manufactured, containing free particles, in the form of aggregate or in the form of agglomerate, of which at least 50% of the particles, in the numerical distribution by size, have one or more external dimensions between 1 nm and 100 nm. [20]
According to the ISO TS 80004-1 standard, a nanomaterial is a material of which at least, one external dimension is at the nanometric scale, that is to say between approximately 1 and 100 nm, or which has an internal structure or nanoscale surface.

1.2.1 Nanomaterials Classification:

1.2.1.1 According to their morphology:

1.2.1.1.1 Materials of dimension 0: materials in dispersed, random or organized form (nanoparticles) as in colloidal crystals for optics or magnetic fluids, they

can be composed of a few tens to a few thousand atoms.

1.2.1.1.2 Materials of dimension 1: materials in the form of nanowires or nanotubes ... of which the nanometric dimension relates to the diameter.

1.2.1.1.3 Materials of dimension 2: materials in the form of a thin layer deposited on a material massive (substrate), as in the deposition of aggregates or the thick coating obtained by plasma spraying or electrochemical means.

1.2.1.1.4 Materials of dimension 3: materials in compact form as in ceramics and nanostructured metals. [21]

1.2.1.2 According to their composition:

1.2.1.2.1 Semiconductor Nanomaterials : In these materials, the electronic structure is constituted for the confinement of the electrons in nanometer-size foils or grains. Due to the quantization of electron energies, these systems are often called quantum structures or quantum dots (QDs) if the electrons are confined by potential barrier in the three spatial dimensions. [23]

1.2.1.2.2 Metal Nanomaterials: These materials are formed by a group of metal atoms with an oxidation state equal to zero. The intense interest in the metallic nanoparticles in different applications such as catalysis or biomedical derives from their unique chemical and electronic properties arising from the small volume to big surface area ratio and their separation in the electronic energy levels providing a specific band structure. [22]

1.2.1.2.3 Metal Oxides Nanomaterials: This group could be enclosed in semiconductor nanocrystals due to their characteristics but they have specific mechanical properties such as low elasticity, high plasticity, low hardness, etc. These nanocrystals

are very important in many areas of chemistry, physics and materials science for the fabrication of microelectronic circuits, sensors, fuel cells. [24]

1.3 Material oxides

1.3.1 Definition

Oxides materials are chemical compounds with one or more oxygen atoms combined with another element (e.g. Li_2O). Oxides are binary compounds of oxygen with another element, e.g., CO_2, SO_2, CaO, CO, ZnO, BaO_2, H_2O, etc. Most of the minerals known on earth are actually oxides and they are very widespread in the universe. Oxides can also be synthesized by oxidation. [26]
Generally, an element is said to be oxidized if it has a positive degree of oxidation, i.e. globally if it is in the form of a cation; however, not all ionic compounds are oxides. The main difference between oxides and other ionic compounds (like salts) lies in the connection between the elements.
Many metals and non-metals react with oxygen to produce metal oxides and non-metal oxides,Therefore,oxides can be divided into this two following in general [27] :

non-metal oxides
like: • sulfur S (in its form sulfur dioxide SO_2 or sulfur trioxide SO3).
- phosphorus P (in its form phosphorous anhydride P_2O_3).
- nitrogen N (in its nitric anhydride NO_5or anhydride form nitrous NO_3).
- carbon C (in its carbon dioxide form CO_2)

metal oxides like : • Titanium dioxide: (TiO_2)
- Tin oxide: SnO_2, tin dioxide.
- Barium titanate: $BaTiO_3$ [28]

1.3.2 Synthesis of Nanoparticulates Oxides

Over the past two decades, new synthesis methods for the production of metal oxide nanoparticles have been routinely reported. These new methods range from no-

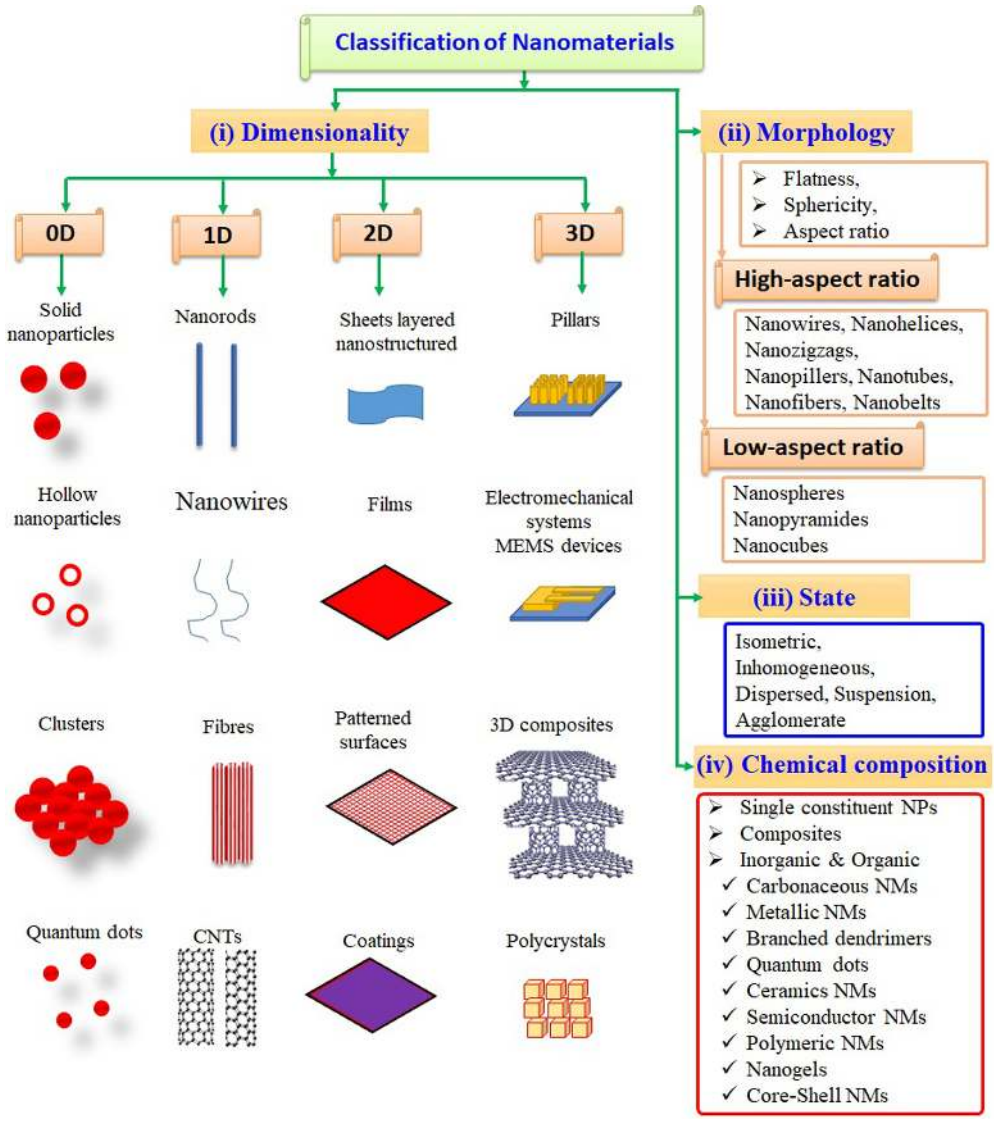

FIGURE 1.2 – Schematic illustration of the classification of nanomaterials based on different criteria. [25]

vel schemes to slight changes to known procedures that provide for the production of a certain desired trait or product. There are several different ways to compare synthesis techniques to evaluate them, such as product yield, product quality, etc. [29]
The first requirement of any novel study of nanoparticulated oxides is the synthesis of the material. The development of systematic studies for the synthesis of oxide nanoparticles is a current challenge and, essentially, the corresponding preparation methods may be grouped in two main streams based upon the liquid-solid and gas- solid nature of the transformations. [30]

1.3.3 Approaches to the synthesis of Oxides Nanoparticles

Manufactured Nanoparticles intended for industrial uses can be synthesized using two different approaches figure 1.3. We differentiate the so-called **"bottom-up"** method from the so-called **"top-down"** method.

Liquid-solid transformations are possibly the most broadly used in order to control morphological characterstics with certain "chemical" versatility and usually follow a **"bottom-up"** approach.
The **"bottom-up"** approach comes from research labs and nanosciences. It consists of building nanomaterials atom by atom, molecule by molecule or aggregate by aggregate. The assembly or positioning of atoms, molecules or aggregates is carried out in a precise, controlled and exponential manner, thus allowing the development of functional materials whose structure is completely controlled.

The "**top-down**" approach stems from microelectronics. It consists in reducing and more precisely in miniaturizing current systems by optimizing existing industrial technologies. The devices or structures are thus gradually undersized or fractionated until they reach nanometric dimensions. High energy grinding is one of the main techniques used in this approach today. [31]
Gas-solid transformation methods with broad use in the context of ultrafine oxide powder synthesis are follow a **"top-down"** approach..

The two approaches tend to converge in terms of the size range of the objects. The **"bottom-up"** approach nevertheless seems richer in terms of type of material,

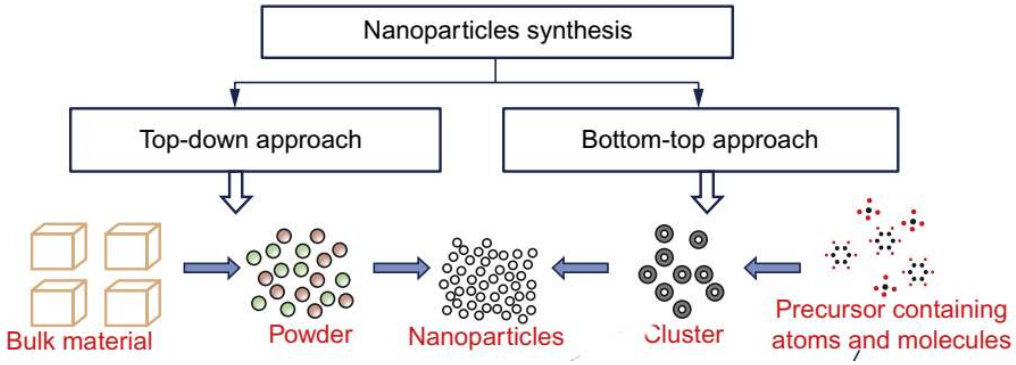

FIGURE 1.3 – Top-down and bottom-up approach for synthesis of Nanoparticles [32]

diversity of architecture and control of the nanometric state, while the **"top-down"** approach makes it possible to obtain quantities of material. more important but the control of the nanometric state turns out to be more delicate.

1.3.3.1 Oxides Nanoparticles synthesis processes:

The current processes allowing the manufacture of nanomaterials are classified into three main categories:

— **Physical processes:**
evaporation / condensation, laser ablation, electric discharge, combustion flames, laser pyrolysis, microwaves, ionic or electron irradiation, catalytic decomposition, physical phase deposition vapor grouped under the term PVD (Physical Vapor Deposition), etc.

— **Chemical processes:**
Vapor phase reactions grouped under the term CVD (Chemical Vapor Deposition) Reactions in liquid medium: chemical co-precipitation, hydrolysis, solvothermal reactions, etc.
Reactions in solid medium, Supercritical fluids with chemical reaction, sol-gel techniques: silica-based sol-gel, metal alkoxide, etc.

— **Mechanical processes:**

High-energy grinding or mechanical synthesis, consolidation and densification, high deformation techniques: torsion, friction, rolling, etc.

• The "**bottom-up**" approach involves chemical and physical development processes, while the "**top-down**" approach primarily involves the use of mechanical methods.

1.3.4 Metal Oxide nanomaterials:

A metal oxide in general is a body made up of metal atoms and oxygen atoms (M1xM2yOz), where M is the chemical symbol of the Metal atom considered, O the symbol of the oxygen atom, " x " and " y " and " z " natural numbers. e.g. Zinc Oxide: ZnO ,Copper Oxides: CuO, copper oxide ,Iron oxides: Fe_2O_3, iron oxide. [26]

We can classify the metal oxides, either according to the nature of the conduction by electrons or by holes(Metal oxides n-types(SnO_2 ;WO_3;ZnO_2...) and p-types(NiO; PdO;La_2O_3...)) , or according to whether the metal oxides are simple(SnO_2, TiO_2, SiO_2,...) or complex($BaTiO_3$, $CaTiO_3$, Mg_2SiO_4, ...).

1.4 Zinc oxide (ZnO):

Zinc oxide is an inorganic compound with the formula ZnO. It's in the form of a white powder broken to odorless pale yellow insoluble in water,As oxide ZnO is safe in case of fire and is relatively inert in contact with the human body. [33]
widely used as an additive in many materials and products such as rubbers, plastics, ceramics, glass, cement, paints and batteries. Zinc oxide is found naturally as the mineral zincite (yellow to red coloring) often containing manganese, but it is largely produced synthetically.
Zinc oxide (ZnO) is a direct wide bandgap semiconductor(3,37 ev). It is transparent in the visible and in the near infrared with an exciton binding energy of 60meV. [34]
Table 1.1 summarizes some of the ZnO properties, Considering that ZnO has several unique properties, it has been used in a variety of applications such as in light emitting diodes , lasers, piezoelectric transducers, varistors, photocatalytic degradation of

environmental contaminants, solar cells, and chemical sensors [35]

TABLE 1.1 – summary of the characteristics of the crystal structure of ZnO [53].

Properties	Characteristic
Crystal structure	Wurtize
Lattice constant (a)	0.325 nm
Lattice constant, (c)	0.521 nm
Density (kg/m^3)	5.6 gcm^{-3}
Exciton binding energy	60 meV
Static dielectric constant (ε_s)	7.9
Optical dielectric constant (ε_∞)	3.7
Optical band gap energy (E_g)	3.2 eV
Flat band potential (E_{fb})	−0.5 V versus saturated calomel electrodes (SCE)
Effective electron mass (M)	0.24–0.3 m_e, $m_e = 9.11 \times 10^{-31}$ kg
Effective hole mass (m_h)	0.45–0.6 m_e $m_e = 9.11 \times 10^{-31}$ kg
Electron mobility (μ_e)	200 cm^2 V^{-1} s^{-1}
Point of zero charge (Pzc)	8–9 pH

1.4.1 Properties of ZnO:

1.4.1.1 Crystal structure of ZnO:

There are three forms of ZnO crystals, hexagonal wurtzite, cubic zincblende, and the rarely observed cubic rocksalt. The wurtzite structure is most stable at ambient conditions and thus most common. [36] The zincblende form can be stabilized by growing ZnO on substrates with cubic lattice structure. In both cases, the zinc and oxide centers are tetrahedral. The rocksalt (NaCl-type) structure is only observed at relatively high pressures about 10 GPa.

Hexagonal and zincblende polymorphs have no inversion symmetry (reflection of a crystal relatively any given point does not transform it into itself). This and other lattice symmetry properties result in piezoelectricity of the hexagonal and zincblende ZnO, and in pyroelectricity of hexagonal ZnO. A more stable state of ZnO is wurtzite structure having hexagonal unit cell with the lattice parameters a = 0.3296, and c = 0.52065 nm. [33]

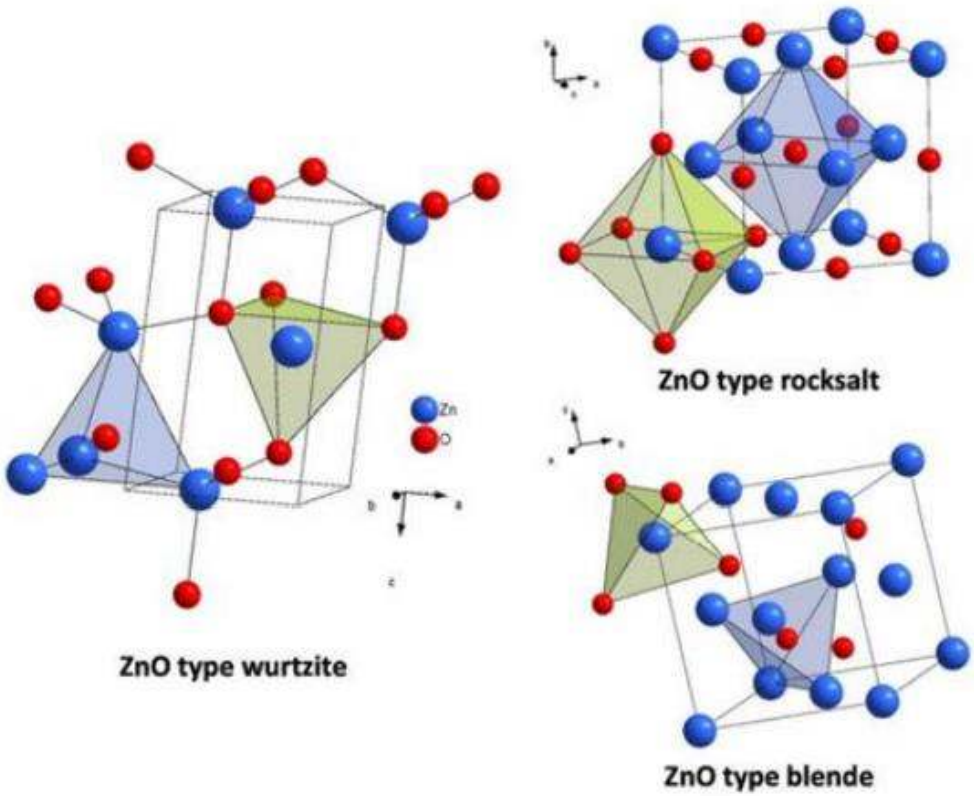

FIGURE 1.4 – the different crystal structures of ZnO (Zinc atoms in blue and oxygen in red)

The oxygen anions and Zn cations form a tetrahedral unit. The entire structure lacks central symmetry. The structure of ZnO can be simply described as a number of alternating planes composed of tetrahedrally coordinated O^{2-} and Zn^{2+} ions, stacked alternatively along the c-axis [37] [38] as shown in the figure 1.4.

1.4.1.2 Optical properties:

The interaction of light (electromagnetic wave) with matter (electrons of the material) can clearly explain the optical properties of a material.

The width of the forbidden band is of the order of 3.37eV, greater than that of conventional semiconductors (Table 1.2), this is a fundamental parameter for light emission type applications (diodes and lasers). It is possible to greatly modify the properties of zinc oxide by doping:

Either by deviating from ZnO stoichiometry, mainly by the introduction of atoms of excess zinc in the interstitial position, or by the creation of oxygen vacancies (the centers created then behave like electron donors) [39] .
Either by substituting the zinc or oxygen atoms of the network with foreign atoms of different valence (element of group III: F^-, Cl^- for example).

TABLE 1.2 – Comparison of the gap of different semiconductors commonly used in the microelectronics industry.

Composé	Si	GaAs	ZnO	GaN
Energie du gap (eV) à 300K	1.12	1.41	3.37	3.20

The refractive index (n) is an important parameter when we want to manufacture optoelectronic systems. The structure of ZnO crystal is of compact hexagonal type, which leads to anisotropy of physical properties. In the case of the refractive index, two different indices are obtained depending on the orientation of the crystal, one noted no (polarization E // at the axis c of the crystal) and the other noted ne (polarization E⊥ at the c axis of the crystal). The refractive index of ZnO in the massive form is 2.0 [40] .

1.4.1.3 Luminescence properties:

ZnO is part of the family of transparent semiconductor oxides in the visible domain thanks to its wide gap, which allows it to be classified among the transparent conductive oxides TCO (transparent conductive oxide) when it is doped. It has a strong absorption and diffusion of ultra violet radiation. Zinc oxide is a transparent material with a refractive index of 2 . [41] . Under the action of a high-energy light beam (E> 3.4 eV) or electron bombardment, zinc oxide emits photons.This phenomenon corresponds to luminescence.
The Photoluminescence (PL) spectra of ZnO structures have been widely reported.In the near ultra violet and in visible regions, due to its wide band gap charater, ZnO

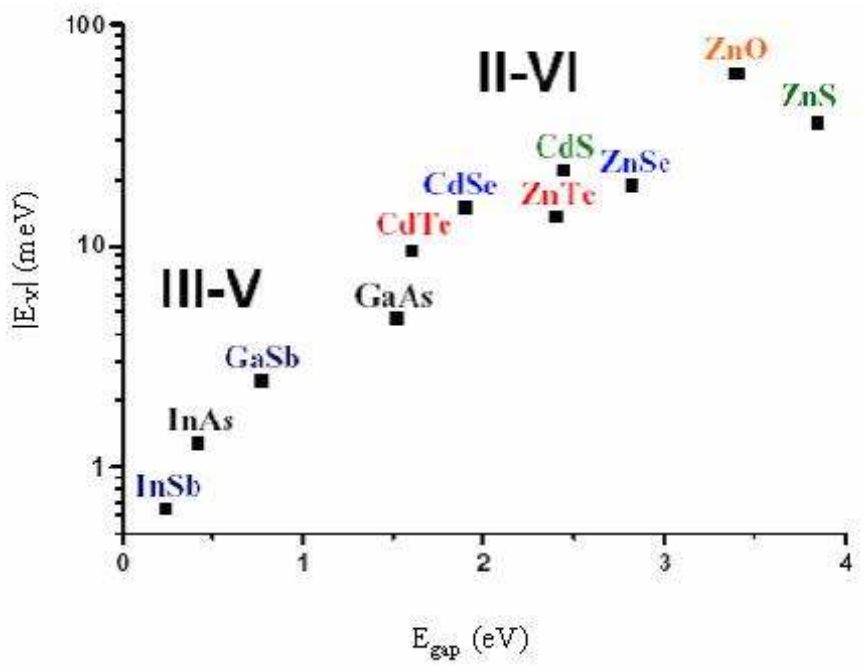

FIGURE 1.5 – Exciton binding energy (free) for III-V and II-VI semiconductors ($m_h^* > m_e^*$)

material dispays uminescent properties, (green radiation with a wavelength close to λ = 550 nm). In layers thin, its refractive index and absorption coefficient vary depending on conditions for the development of layers. figure 1.5
Since luminescence is dependent on the doping of the material [42] , this property is used in optoelectronic devices such as cathode ray tube displays, light emitting diodes for color displays, signaling or lighting.

1.4.2 Present and Future Applications Of zinc Oxide

Among metal oxides, zinc oxide has sparked intensive research efforts to its unique and useful properties in various fields of application.
Historically, ZnO has been used, first for its piezoelectric effect as transducer in wireless radio receivers in the 1920s, before booming considerable in the 1970s in the fields of the chemical industry and pharmaceutical (paint, sunscreens, etc.). Since the 2000s, most of of the global production of zinc oxide, synthesized in nanoscale powder, is used in the rubber and tire industry (57% of the market) as a catalyst in the vulcanization process, chemicals, paints for its protection against UV, agriculture, ceramics

and photovoltaic solar cells as a window optical (conductive transparent oxide: OTC) . The catalytic properties of ZnO also give rise to great interest in recent years, particularly in the field of water pollution control. From therefore, ZnO is one of the most promising functional materials due to the technical progress made in terms of synthesis, its intrinsic properties (catalytic, optoelectronic and electrical) and its various morphologies. Among his various fields of application, only the field of photocatalysis is developed in the continuation of this study. [43]

1.4.2.1 Present Applications

1.4.2.1.1 Cement, Rubber, Paint and Glazes ZnO serves in large quantities as additive to cement or concrete. It prolongs the cement setting time and improves the hydraulic properties. As an additive to rubber, it improves the rubber cure.Because of its high heat conductivity, it contributes additionally to the transport of heat e.g. out of tires resulting from the crunching.
ZnO is a white pigment used in paints, also known as Chinese white. In contrast to (e.g.) Pb containing pigments, it is not poisonous, does not react with H_2 Sand does not change its colour under illumination. Partly, TiO_2 is replacing it nowadays. Furthermore, ZnO can be added to the glazes of ceramics. [33]

1.4.2.1.2 Catalysts, Pharmaceutics, Cosmetics and Food Additives Because of its high absorption over the whole UV spectral range and its good hoto stability, ZnO is used as absorber in sun blockers, but also in other cosmetics and pharmaceuticals. ZnO is known to have anti-inflammatory and bacteriostatic properties. Therefore, it is used in cremes, ointments and on fabrics [44].
It is also found as an additive to human and animal food to compensate Zn deficiencies in nutrition. A nano rod has been used successfully to measure the membrane potential across a human fat cell or the intracellular pH value .

1.4.2.1.3 Gas Sensors It is also known sincemore than half a century that the surface conductivity of ZnO can be stronglymodified by the surrounding gas atmosphere, for example by oxygen or hydrogen.These gases are adsorbed to the surface and shift the Fermi levelwith respect to the bands.
In this sense, the action as catalyst is rather directly connected with the sensor application. Some more recent reports on applications of ZnO as gas sensor are given

in [45] [46] . One idea is to use ZnO nano rods because of their huge surface-to-volume ratio .Other developments aimat selective coatings of the surface of ZnO, which allow the docking of specific molecules only. This concept can be extended even into the range of ZnO-based biosensors.
Partly as a point of curiosity, it should be mentioned that not only the surface conductivity can be changed by an ambient gas but also the luminescence yield . This effect will also allow an optical reading of such sensors.

1.4.2.1.4 TCO, Solar Cells Applications ZnOcan be easily n-type doped reaching electron concentrations beyond 1020 cm?3. The doping is generally on the Zn site with Al, Ga or In.. Doping with halides on the anion site is very efficient in other II–VI com pounds like ZnSe but has been less investigated in ZnO. These highly n-doped samples are essentially transparent in the visible, but bulk, highly Ga-doped samples show a slight bluish colour presumably . These highly dopedwide band gap semiconductors are generally called transpar- ent conducting oxides (TCO).
The ZnO-based TCOs can be produced by many square meters (e.g.) by stuttering. They serve (e.g.) as transparent front contacts for solar cells, liquid crystal displays, in MESFETS or as heat protecting and energy saving coatings for windows, which transmit the visible but reflect the IR. Concerning photovoltaic, early examples of aqueous systems with ZnO electrodes ZnO does not only serve as contact material , but also as a functional one, for example in hybrid solar cells made from n-type ZnO and a p-type semiconductor like Cu_2O or from ZnO nano particles and conjugated polymers.
Alternatively, ZnO nano wires can be used in dye sensitized solar cells. In any case, a medium is necessary to extend the absorption spectrum towards longer wavelengths.

1.4.2.2 Visions of Future Applications

1.4.2.2.1 pn Junctions for ZnO-based semiconductor pn junctions .The n-type region can be easily made from ZnO/X with X D Al, Ga or In. Since first reliable reports on p-type doping have been published recently, ZnO homo junctions have been produced. The other possibility is to grow heterojunctions with n-type ZnO, its alloys or ZnO-based quantum wells and a p-type doped semiconductor such as SiC, Si, GaN, GaAs, NiO, $SrCu_2O_2$,$CuCrO_2$,$ZnRh_2O_4$ or even a p-type organic semiconductor. One has to ask, however, in the case of heterojunctionswhy one should use n-type ZnO with p-type GaN, since n-type $In_{1-x}Ga_xN$ is also readily available.

For LEDs there are both arguments in favour of and drawbacks for heterojunctions . Recently, non-volatile memory devices based on resistance switching including ZnO-based selector elements have been suggested as an application of Schottky or pn junctions . One of themain advantages is said to be the ability to stack these cross-bar memory structures in three dimensions, since there is no need for single crystallinity, such as in silicon. In such a cross-bar memory, a selector element as well as a memory element needs to be realized. As a selector element, a ZnO-based Schottky diode or p-n-diode can be used. For the bit storage element, resistance switching has been demonstrated in another oxide semiconductor,NiO. InNiO, different conduction paths are created after employing high current densities, leading to a reversible resistance switching.

1.4.2.2.2 Light Emitting Diodes The most important aspect that drives the present renaissance (or hype) of ZnO research and development (R and D) is the hope to obtain with ZnO a material alterna- tive to or instead of group III-Nitrides for a blue optoelectronics.More specifically, light emitting diodes (LED) or even laser diodes (LD) aremeant fromthe green over
the blue to the near UV spectral range using the combination Zn1-xCdxO=ZnO in the first case and the combinations $Zn_{1-x}Mg_xO$=ZnO or $Zn_{1-x}Be_xO$=ZnO in the second.

1.4.2.2.3 Field Emitters The pointed tips of etched or as-grown, needle-like bulk ZnO crystals enhance the electric field strength if a voltage is applied between the ZnO needle and a counter electrode in vacuum. This fact triggered rather early the idea of field emission from ZnO.
For an early experimental realization. Therefore, it is not surprising that the idea came up again with the availability of nano rods, which have a tip with a small radius of curvature. As a further application-friendly aspect, these nano rods grow in well-defined places on pre-structured substrates. Besides the interest- ing physics and material properties, which can be learned from this effect like the density of surface states, the idea came up to use ZnO nano rods as field emitters in flat panel displays by accelerating the field emitted electrons onto a phosphor screen. The questions, which have to be answered before a large-scale application becomes possible, concern again the lifetime or degradation of the rods. ZnO is a relatively soft material compared (e.g.) with tungsten, and degradation has been seen even for bulk samples at rather low currents.

1.4.3 The doped ZnO

The properties of ZnO nanocrystals can be efficiently tailored by doping of suitable element into the host matrix for a wider range of possible applications.
Generally, it is possible to dope the matrix of ZnO with metallic elements according to the desired physical properties. We can cite for example:
Al, In, Ga, Mo, Eu, Er, Yb,... for the optoelectronic properties;
Fe, Co, Mn,... for the magnetic properties:

1.4.3.1 ZnO doped with transition metal

1.4.3.1.1 Ion Copper Copper is a chemical element with the symbol Cu (from Latin: cuprum) and atomic number 29. It is a soft, malleable, and ductile metal with very high thermal and electrical conductivity. A freshly exposed surface of pure copper has a pinkish-orange color. Copper is used as a conductor of heat and electricity, as a building material, and as a constituent of various metal alloys, such as sterling silver used in jewelry, cupronickel used to make marine hardware and coins, and constantan used in strain gauges and thermocouples for temperature measurement.
it belongs to the group 11,period 4 ,d-block of the periodic table as well as to family of transition metal.

Chapitre 2

Synthesis and cracterizations techniques of Cu doped ZnO nanoparticles

In this chapter, we present the different Synthesis and Characterization techniques used in our work, particularly we describe the solvothermal methode that used in our work. Characterization methods of as synthesize Cu-doped nanopwders were discused, include X-rays diffraction (XRD), The Fourier-transform infrared spectroscopy (FTIR) and thermogravimetric and differential thermal analysis(TG/DTA).

2.1 Solvothermal method

2.1.1 Brief History of the Hydro/Solvothermal Technique

The emergence and development of the solvothermal/hydrothermal process is closely linked to the development of nanomaterial. The first report about the hydrothermal process could be traced back to the middle of the nineteenth century, when it was employed to prepare sub micrometer to nanometer-sized quartz particles. However, the research and application of the hydrothermal process in material synthesis lagged from 1840s to the early 1990s because techniques to characterize nanoscale products were not available and, to some extent, because knowledge of hydrothermal solution chemistry was insufficient to successfully realize the control of crystal growth. Hydro-

thermal techniques revived in 1990s along with the revolution in nanoscale materials and the emergence of high-resolution microscopes from 1980s.
Simultaneously, great progress was achieved in understanding chemical and physical properties of hydrothermal systems, which led to development of the solvothermal process, in which organics were introduced as solvents in manufacturing well-controlled nanomaterials. In the twenty-first century, the hydrothermal/solvothermal process has gained great successes in manufacturing nanomaterials with crystallinity, crystal phase, morphology, and size control, due to its outstanding advantages, including low process temperature, performance of reactions in liquid environments, low energy consumption, and environmental benignity [47] .

2.1.2 Definition of Hydrothermal/Solvothermal Process

A hydro/ solvothermal processes can be defined as a processes in a closed reaction vessel inducing a decomposition or a chemical reaction(s) between precursor(s) in the presence of a solvent at a temperature higher than the boiling temperature of this solvent. The pressure can be autogeneous or imposed (the pressure value being higher than 1 bar (105 Pa) at the starting point of the experiment through the compression of the reaction medium).
Depending on the experimental conditions (pressure and temperature), it will be increase the solvent's ability to dissolve solids and speed up reactions between solid species. In a typical procedure, the pre- cursors and other reagents, including the solvent, are loaded in appropriate ratios into an autoclave, which is placed in an oven at a set temperature for a fixed period. The sample is washed with water and alcohols to remove impurities and then vacuum-dried before the final product can be obtained [50].
The solvothermal system can be heterogeneous or homogeneous and in subcritical or supercritical conditions [51].
The solvothermal method is analogous to the hydro- thermal method, except that organic solvents, instead of water(Originally, such processes were developed with water, due to its importance on the surface of the earth.), are used in the synthetic procedure. The word "solvothermal" can be used whatever the chemical composition of the solvent is (aqueous or non-aqueous. Alternatively, the reactions are called alcohothermal and glycothermal, respectively, when alcohols and glycerol are used as the reaction

media. These synthetic strategies are important for the preparation of NCs with good crystalline properties, [50]
The interest of hydrothermal/solvothermal reactions in a large domain of applications (materials synthesis, crystal growth, thin films deposition, low temperature sintering...) has improved the development of new processes involving original technologies as hydrothermal- electrochemical methods, microwave-hydrothermal method... Chemical reactions into a solvent (aqueous or non-aqueous) under high pressure and mild temperature conditions (sub- or supercritical domain of the selected solvent) appear promising for developing Materials Chemistry and Materials Sciences (in particular for nanotechnologies). [52]

2.1.2.1 The parameters of solvothermal synthesis

Taking into account the definition of a solvothermal process, the factors playing a key role can be divided into different classes.

- **Physical processes:**
  - The chemical nature of the solvent and its physico- chemical properties,
  - The chemical composition, structure and properties of the precursors,
  - The nature of the additives, and the pH value of the reaction medium.

- **Thermodynamical factors**
  – The temperature.
  – The pressure.

- **The associated technologies employed**
  – Microwaves,
  – Electrochemistry,
  – Externalmagnetic field,
  – Ultrasound, and others. [51]

2.1.2.1.1 Factors controlling the mechanisms of chemical reactions During the last years the mixing mode of the reactants and its impact on the reaction mechanisms characterizing solvothermal processes have been investigated, as for example:
– Solvothermal pressure relief where the amount of gas produced in the high-pressure

vessel is controlled
– Solvothermal scission-template-transportation with the formation of an intermediate compound acting as a template,
– Solvothermal extraction,
– Phase-transfer catalysis,
– High-temperature mixing method. [51]

2.1.2.2 Development of solvothermal reactions

2.1.2.2.1 Reactions involved in solvothermal processes: Solvothermal reactions involve "in situ" different reaction-types as mentioned through the analysis of the chemical factors governing such processes. In particular, it is possible in a first approach to classify the reactions in approximately 5 types:
(i) oxidation-reduction, (ii) hydrolysis, (iii) thermolysis, (iv) complex-formation, (v) metathesis reactions.
The development of these different reactions implies to control carefully the chemistry in non- aqueous solvents and consequently to get more informations concerning the physico- chemical properties of such solvents. [52]

2.1.3 Instruments Used in Hydro/Solvothermal Synthesis:

2.1.3.1 Autoclave:

Most hydrothermal/solvothermal reactions proceed in a sealed reactor, known as an autoclave, a pressure vessel, or a high-pressure bomb. In most cases, hydrothermal/ solvothermal reactors are metal autoclaves with Teflon or alloy linings or containing an extra can, beaker, or tube made of Teflon, platinum, gold, or silver to protect the autoclave body from the highly corrosive solvent, which is held at high temperature and pressure. In some cases, a Bourdon gauge is fixed to the autoclaves to directly monitor the pressure, and the autoclaves are equipped with stirring accessories to minimize the concentration gradient inside them. In addition, an ideal hydrothermal/solvothermal autoclave should be easy to assembly our disassembly, as well as be leak-proof and possess sufficient running life within the experimental temperature and pressure range.

Figure 2.1 shows the most popular general-purpose autoclave used in laboratories. The reactors commonly used in hydrothermal/solvothermal processes. The working

conditions of autoclaves vary for different materials, including glass, quartz, and high-strength alloys. Temperature, pressure, and corrosive resistance of reactor materials are the most important parameters for the reactor selection. For safety, pressures generated in a sealed vessel should always be estimated and controlled below the strength of autoclave materials. [47]

An ideal hydrothermal autoclave should have the following characteristics:

- Inert to acids, bases and oxidizing agents.
- It should be easily assemble and dissemble.
- It should have sufficient length to obtain a desired temperature gradient.
- It should be leak-proof at desired temperature and pressure.
- It should bear high pressure and temperature for long duration of time. [48]

The top-priority parameter to be considered in selecting a suitable autoclave is the experimental pressure and temperature conditions and the corrosion resistance in a hydrothermal solution. In accordance with the above, the materials, thick glass cylinders, thick quartz cylinders, and high strength refractory alloys are usually used to fabricate hydrothermal autoclaves. Some hydrothermal reactions, in which the reagents or solvents are noncorrosive, can take place directly in the hydrothermal autoclaves [49] like in our work.

2.1.4 Advantage and Disadvantage of hydrothermal/solvothermal synthesis

2.1.4.0.1 Advantages of hydrothermal/solvothermal synthesis :

- Most material can be made soluble in a proper solvent by heating and pressuring the system close to its critical point.
- Significant improvement in the chemical activity of the reactant, the possibility to replace the solid-state synthesis, and materials which may not be obtained via solid-state reaction may be prepared through hydrothermal/ solvothermal synthesis.
- Products of intermediate state, metastable state, and specific phase may be easily produced, novel compounds of metastable state and other specific condensed states may be synthesized.
- Easy and precise control of the size, shape distribution, and crystallinity of the final product through adjustment of the parameters, such as reaction temperature, reaction time, solvent type, surfactant type, and precursor type.

FIGURE 2.1 – A general-purpose hydrothermal/solvothermal autoclave.

- Substances with low melting points, high vapor pressures, and that tend to go pyrolysis will be obtained. [52]

2.1.4.0.2 Disadvantages of hydrothermal/solvothermal synthesis :

- The need for expensive autoclaves.
- Safety issues during the reaction process.
- Impossibility of observing the reaction process ("black box"). [52]

2.1.4.1 Main applications of solvothermal synthesis:

Solvothermal reactions have been developed in different scientific domains :

- The synthesis of novel materials (design of materials with specific structures and properties),
- The processing of functional materials (an emerging route in synthesis chemistry),
- The crystal growth at low-temperature (a way to single crystals of low-temperature forms or with à low density of defects),
- The preparation of micro- or nanocrystallites well define in size and morphology (as precursors of fine structured ceramics, catalyst, elements of Nano-devices. . .),
- The low- temperature sintering (preparation of ceramics from metastable structural forms, low temperature forms or amorphous materials),
- The thin films deposition (with the development of low-temperature processes)

Such a paper being devoted to the development of solvothermal reactions in Materials Chemistry a specific attention will be given to the synthesis of novel materials and the development of new processes. [52]

2.1.4.2 Synthesis of Nanomaterials via Hydrothermal and Solvothermal Methods

Nanostructured materials with controllable size, shape, crystallinity, and tunable surface functionalities have attracted extensive research attention due to their unique optical, electronic, magnetic, mechanical, and chemical properties, which are derived mainly from the quantum confinement effect and large surface to volume ratios. The hydrothermal and solvothermal synthetic methods are considered to be among the most promising approaches to preparing nanomaterials. In recent years, a tremendous number of nanomaterials have been processed by hydrothermal or solvothermal me-

thod and thousands of science papers about the hydrothermal/ solvothermal synthesis of nanomaterials have been published.These methods possess many advantages, such as producing a large amount of nanomaterials at a relatively low cost and yielding highly crystalline nanocrystals (NCs) with well-controlled dimensions. From the perspective of morphology of nanomaterials, the hydrothermal technique has been used to process nanomaterials with a variety of morphological features, such as nanoparticle, nanosphere, nanotube, nanorod, nanowire, nanobelt, nanoplate, and so on. From the perspective of composition of nanomaterials, the hydrothermal technique can be used to process almost all types of advanced materials like metal, alloy, oxides, semiconductors, silicates, sulphides, hydroxides, tungstates, titanates, carbon, zeolites, ceramics, and a variety of composites. The hydrothermal or solvothermal technique is not only used to process simplest nanomaterials, but also acts as one of the most attractive techniques for processing nanohybrid and nanocomposite materials. In short words, the great advantages of hydrothermal technology for nanomaterials processing are the production of particles that are monodispersed with total control over their shape and size in addition to their chemical homogeneity with the highest dispersibility. [49] [47]

2.1.4.3 Recent Trends in Solvothermal Processes According

According to literature, different research domains have been strongly involved in the development of solvothermal processes.

- Synthesis of novel materials:

During the last twenty years mainly oxides, fluorides or nitrides have been prepared through solvothermal routes .New preparation methods have recently been developed, in particular for the synthesis of sulfides, the elaboration of oxynitrides, and to set up fluorination processes. In addition, a strong interest has been focused on the solvothermal synthesis of carbon, in particular carbon sheets, carbon nanotubes and graphene.

- Development of new solvents

Ionic liquids appear to be functional solvents for the preparation of nanocrystallites due to their specific physico-chemical properties and their use as potential templating and structure-directing agents. In addition, different bi functional solvents have been developed as complexing and reducing agents (in particular to stabilize metallic nano

particles).

- Elaboration of nano crystallites

Nanocrystallites well defined in size but with Specific morphologies, in particular nanophosphors, nanotubes and nanocomposites, have attracted great interest in recent years.

- Solvothermal processes in biochemistry

the impact of hydrothermal reactions in biochemistry is an important challenge either for a better understanding of the origin of life or for the development of new original routes to biomolecules.

- Synthesis of hybrid materials

Hybrid materials such as inorganic/organic, with an emphasis on the stabilization of novel structures, or inorganic/biological, with specific properties, represent an important challenge for the future.

- Development of hydro/solvothermal crystal growth processes

The preparation of single crystals for functional materials is always an important domain for various industrial applications. In particular GaN and ZnO have received increasing interest from both fundamental and technological points of view.

- Preparation of thin films through solvothermal processes

During the last years, solvothermal routes have been developed to thin films using different types of substrates to produce particles of good homogeneity in size and morphology. [51]

2.2 Experimental protocol

2.2.1 Preparation of pure ZnO and ZnCuO Nanopowders

ZnO and $Zn_{1-x}Cu_x$ O nanopowder (x=0.01, 0.03, 0.05 and 0.07) were prepared by the Solvothermal method using zinc diacetate as a source of zinc and copper nitrate source of steroids.

First, the synthesis steps of pure ZnO nanoparticles prepare a homogeneous solution through Dissolve an amount of acetate Hydrated zinc $Zn(CH_3COO)_2.2H_2O$ in V volume of alcohol, with stirring magnetic at 40 °C for 20 minutes.

second, In the exemplary process of prepration Cu doped ZnO . zinc diacetate and copper nitrate were dissolved according to their stoichiometry in the fifth volume of ethanol. Both were mixed thoroughly and stirred with a magnetic stirrer at 40 °C for 15 min.

An amount of ethanolamine is added to the prepared solutions, then the solution is transferred to anstainless steel metal enclosure (autoclave), then closed and heated at a temperature of 130 ° C for 4 hours.
The resulting precipitate was successively washed with distilled water and alcohol. After the cleaning step, the precipitate is dried at 80 °C for 24 hours, to remove the rest of the water and ethanol and finally to obtain the desired nanopowders.

2.3 Characterization Techniques :

2.3.1 X-ray diffraction:

In materials science, X-rays diffraction is known as a characterization technique capable of investigating the crystalline structures of the grown nanostructures. This non-destructive analytical technique is quite useful for studying chemical composition, crystal structures and their phases, size, symmetry of the unit cell, lattice constants of nanoparticles and physical properties of grown materials.

2.3.1.1 Diffractometer of X-rays

The prepared samples were examined by X-ray diffraction (XRD) analysis using a PANalytical X'Pert Pro diffractometer from Mohamed Boudiaf M'sila University, using the k_α line of copper for a wavelength λ= 1.54060Å. The diffractograms were acquired in θ - 2θ geometry for an angular range of 2θ to 80 °C. X-ray diffraction characterization is a crucial step in determining the purity and crystallinity of materials after synthesis. It's based on the diffraction of X-rays by matter. The general method

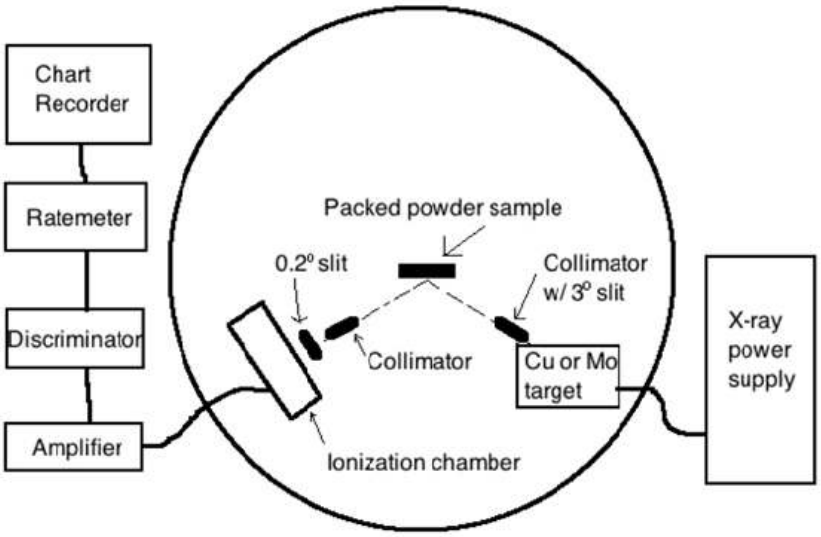

FIGURE 2.2 – Typical block diagram of X-ray diffractometer

consists in bombarding the sample with X-rays, and in analyzing the intensity of the X-rays, which is scattered according to the orientation in space. Scattered X-rays interfere with each other, the intensity therefore has maxima in certain directions, we speak of a "diffraction" phenomenon. The intensity detected is recorded as a function of the deflection angle 2θ of the beam. [53]

X-ray diffraction spectra analysis

X-ray diffraction spectrum is a recording of the diffracted intensity as a function of the angle $2\theta_{hkl}$ formed with the incident beam. It makes it possible to obtain a great deal of many informationes especially on structural properties: crystallization (or not), presence of parasitic phase (s), crystallographic parameters, orientation and grain size (inversely proportional to the width at mid-height of the lines diffraction). [54]

2.3.1.1.1 Bragg's law Principle: The diffraction phenomenon results from the interaction of an electromagnetic wave, such as than X-rays, with the periodic medium of crystallized matter. X-ray diffraction of powdered samples (known as "X-ray powder diffraction") is commonly used for the characterization of solids. The term powder simply means that the incident X-ray beam is sent onto a set of crystallites, randomly oriented, sufficiently numerous for all the orientations to be achieved.

FIGURE 2.3 – X-ray Diffractometer of Msila University

When a monochromatic x-ray of wavelengthλ is sent to a sample with an angle of incidence θ, the reticular planes (hkl) of the crystal, equidistant from dhkl (inter-reticular distance), will behave like parallel mirrors and reflect the electromagnetic wave, inducing a diffraction phenomenon. The diffracted intensity will be non-zero only if the contributions of the successive planes are in phase (constructive interference), that is to say if Bragg's law is respected:

$$n\lambda = 2d_{hkl}sin\theta \tag{2.1}$$

Such as: dhkl represents the inter-reticular distance of the crystal lattice.
λ is the wavelength of the incident beam.
n is an integer that represents the order of the reflection.

θ represents the angle of incidence of the X-rays with respect to the surface of the sample. [55]

2.3.2 Fourier transform infrared spectroscopy FTIR

2.3.2.1 Infrared radiation

Infrared radiation, is a type of electromagnetic radiation same as that of radio waves, UV light rays, visible light, X-rays, and gamma rays [56] Table2.1.
It lies between the visible end of the light spectrum, and the microwave spectrum. Invisible to the eye, it can be detected as a sensation of warmth on the skin. The infrared range is usually divided into three regions: near infrared (nearest the visible spectrum), with wavelengths 0.78 to about 2.5 micrometres.

2.3.2.2 Analysis by infrared spectroscopy (IR):

Principle :

A sample is subjected to electromagnetic radiation in the infrared region of the spectrum. The wavelengths that are absorbed by the sample depend on the nature of the chemical groups present. These wavelengths are defined by a wave number (cm^{-1}) that is obtained by dividing the number 10000 by the wavelength in microns.2.4

FIGURE 2.4 – FTIR-8300 instrument of Msila University

Modern infrared spectrometers use Fourier transform for the calculation of results. The method is called Fourier transform infrared spectroscopy, abbreviated as FTIR. This method makes it possible to detect characteristic vibrations of bonds and to analyze the chemical functions present in the material. When the wavelength provided by the light beam is close to the energy of the molecule, the latter will absorb the radiation and there will be a decrease in the reflected or transmitted intensity. The infrared range between (2.5-25 μm) corresponds to the vibrational energy range of molecules. [59]

TABLE 2.1 – Comparison of Average Sample Depth for Various Surface Analysis Techniques [57]

Analysis Method	Sampling Depth
- Fourier transform infrared spectroscopy (FTIR), Raman spectroscopy, conventional secondary ion mass spectroscopy (conventional SIMS)	<2 mm
- Energy dispersive X-ray (EDS or EDAX)	<5,000 Å
- Rutherford back scattering (RBS)	<400 Å
Surface secondary ion mass spectroscopy (surface SIMS)	<300 Å
- Electron spectroscopy for chemical analysis (ESCA) also called X-ray photoelectron microscopy (XPS)	<100 Å
- Auger electron spectroscopy (AES)	<100 Å
- Ion scattering spectroscopy (ISS), also called low-energy ion scattering (LEIS)	<2 Å
- Time-of-flight secondary ion mass spectroscopy (TOF-SIMS)	1.3 Monolayers
- Atomic force microscopy (AFM) or scanning probe microscopy (SPM)	0.1 Å

Not all vibrations give rise to absorption, this will also depend on the geometry of the molecule and in particular on its symmetry. For a given geometry, we can determine

the active modes of vibration in infrared thanks to the Group Theory. The position of these absorption bands will depend in particular on the difference in electronegativity of atoms and their mass. [59]

2.3.3 Thermal analysis (DTA/TG):

The thermogravimetric analyzes of our samples of ZnO pure and Cu doped ZnO nanoparticles have been carried out using SETARAM: LabSys evo instrument (figure 2.5), equipped with a SETARAM TGA 1600 thermobalance with two symmetrical ovens and different measuring rods TG and ATD. Samples were heated from 30 ° C to 800 ° C under argon with a ramp of 20 ° C / min.

Thermogravimetric analysis (TG) or thermogravimetry (TG) is a technique for the measurement of thermal stability of materials. where changes in the weight of a specimen are measured while its temperature is being increased. Moisture and volatile contents of a sample can be measured by TGA.
A TGA consists of a sample pan that is supported by a precision balance. That pan resides in a furnace and is heated or cooled during the experiment. The mass of the sample is monitored during the experiment. A sample purge gas controls the sample environment.

This gas may be inert or a reactive gas that flows over the sample and exits through an exhaust. TG apparatus is equipped with a microfurnace, which can be rapidly cooled. The heating element is made of platinum (reliable up to 1000 C°). Mass loss may be categorized as volatile components such as absorbed moisture, residual solvents, or low - molecular - mass additives or oligomers that generally evaporate between ambient and 300 ° C; reaction products, such as water, which generally form between 100 ° C and 250 ° C; and generation of volatile degradation products resulting from chain scission that generally require temperatures above 200 ° C but not more than 800 ° C. All of these mass loss processes may be characterized by TG to yield information such as composition, extent of cure, and thermal stability. The kinetics of these processes may also be determined to model and predict cure, thermal stability, and aging due to thermal and thermooxidative processes. [62] [61] [60]

FIGURE 2.5 – TG/DTA SETARAM: LabSys evo instrument of Msila University

Chapitre 3

Results and discussion

In this chapter we present and discuss the results obtained from the structures properties of ZnO and Cu-doped ZnO (x = 0.01, 0.03, 0.05 and 0.07) nanopowders prepared by Solvothermal technique.

3.1 XRD – Structural studies

X-ray diffraction analysis was used to study the structural properties and the phase purity of the samples. Figure 3.1 illustrates the XRD patterns of pure and Cu-doped ZnO nanoparticles obtained by solvothermal route at 130°C.
All the diffraction peaks in the patterens could be indexed as the hexagonal wurtzite structure of ZnO, which were consistent with the values in the standard card (JCPDS there are in good agreement with PDF Code: 00-036-1451 and confirm the wurtzite hexagonal structure of solvothermal synthesized nanoparticles. The peaks at 2θ values of 31.78°, 34.42°, 36.25°, 47.85°, 56.524°, 62.882°, 66.47°, 67.98°, 69.11°, 72,70°, 76.982°, corresponding to planes (100), (002), (101), (102), (110), (103),(200) (112), (201), (004), (202) respectively. This results confirme that the Cu doped ZnO nanopowders with high cristallinity were successfully synthesized by the solvothermal method.

As can be seen from x-ray patterens, no signal of Cu related phase such as metallic copper, oxides of copper, or any binary zinc copper phase is identified for x = 0.01/0,03/0,05 samples and no characteristic peaks were observed for the other impurities. This can be explain that the Cu ions have substituted Zn sites without

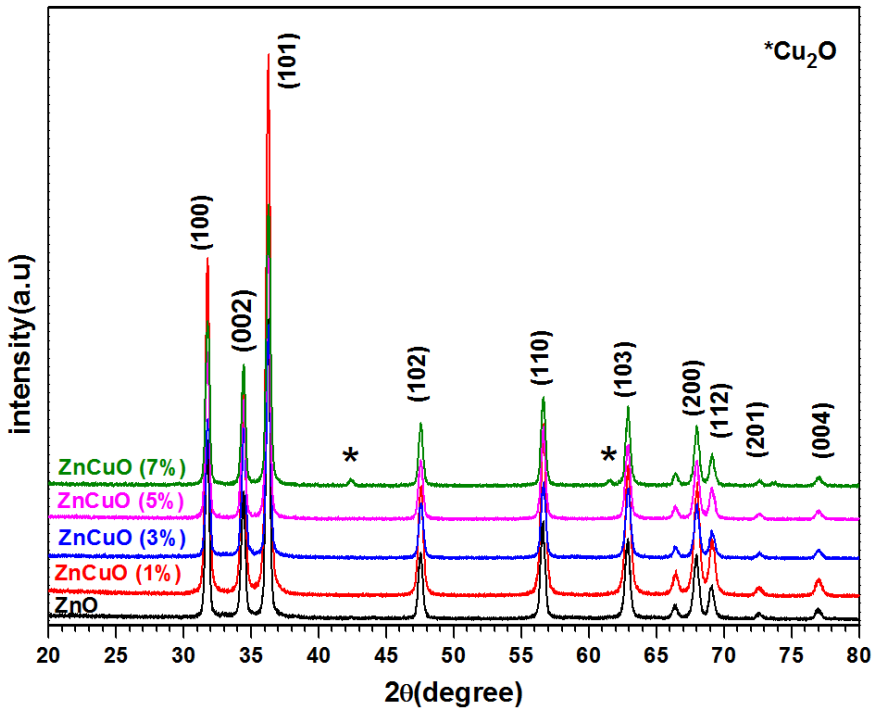

FIGURE 3.1 – XRD patterns of pure and Cu-doped ZnO nanoparticles synthesized by solvothermal method

considerably altering the crystal structure of ZnO, which is associated to the fact that the ionic radius of Cu (0.73 Å) is very close to that of Zn^{+2} (0.74 Å). By increasing the doping percentage of Cu (x = 0.07), two peaks corresponding to Cu_2 O appears. The extra Cu atoms might also not occupy the correct places inside the ZnO crystallites because of the limited solubility of Cu inside ZnO. The ionic radius of Cu is smaller than that of zinc and the excess Cu may occupy interstitial positions and deform the crystal structure.

-

3.1.1 The Comparison between Un-doped and Zn $_{1-x}$Cu$_x$O (X=0,07):

The XRD patterns of the as-prepared pure ZnO and Cu-doped ZnO nanparticles (Zn $_{1-x}$Cu$_x$O (X=0,07) are shown in Fig. The well-defined diffraction peaks in the XRD diagram clearly shows the crystalline character with peaks corresponding to

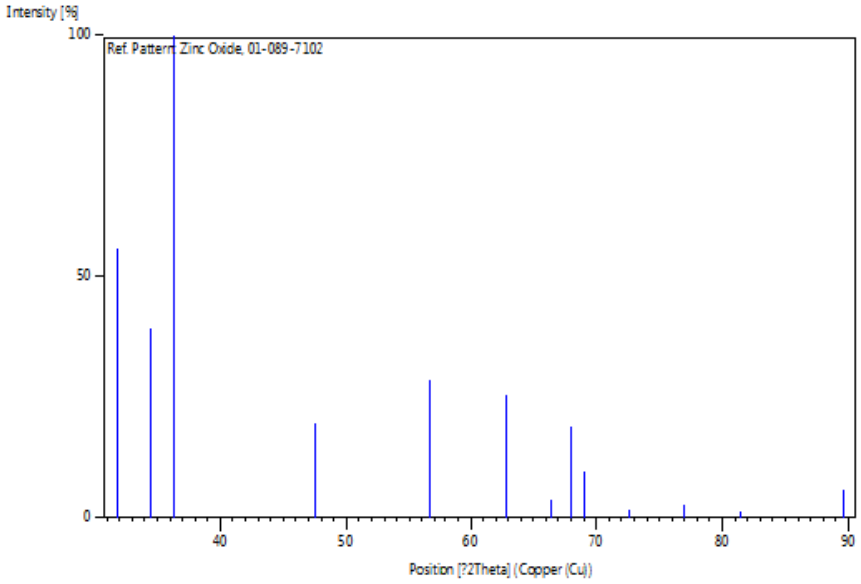

FIGURE 3.2 – The X-ray diffraction diffractogram of ZnO [01-070-2551].

(100), (002), (101), (102), (110), (103), (200), (112),(201) and (004) planes according to the standard PDF Code: 00-036-1451 and is indexed as the hexagonal wurtzite with preferred orientation along (101) plane in the samples.

According to XRD pattern of $Zn_{1-x}Cu_xO$ (X=0,07) sample, additional peaks are observed at $2\theta = 42.41°$, and 61.50° which are related to the planes (200) and (220) of Cu_2O phase with cubic structure (JCPD no. 77-0199).

Structural parameters (such as lattice parameters, bond length and unit cell volume) are extracted from X-ray diffractograms and are tabulated in Table 3.1

So as we sad When an X-ray beam having wave length λ strikes the solid crystal with an angleθ ,the resulted scattered radiation can be determined by virtue of Bragg's law 3.1 [65]:

$$n\lambda = 2d_{hkl}sin\theta \tag{3.1}$$

Where n is called the diffraction order and d denotes the distance in between the diffracting planes in the Miller indices (hkl). Remember that the set of d planes is

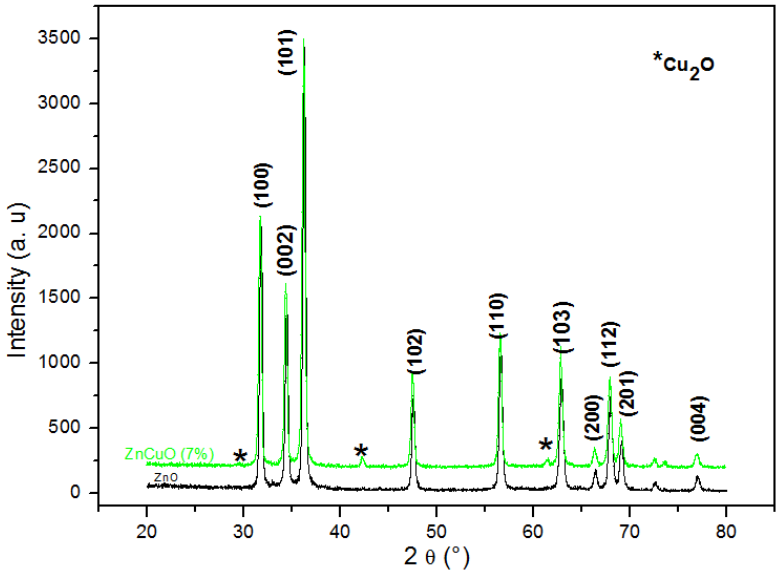

FIGURE 3.3 – X-ray diffractogram of ZnO and Zn $_{1-x}$Cu$_x$O (X=0,07) nanoparticles, synthesized by the solvothermal method.

unique for each material.
the relation between the inter-reticular distance and lattice parameters as well as Miller indices In the hexagonal wurtzite structure of ZnO is given by 3.2 [66]:

$$\frac{1}{d_{hkl}^2} = \frac{4}{3}\frac{(h^2+k^2+hk)}{a^2} + \frac{l^2}{c^2} \tag{3.2}$$

With the first order approximation, n = 1

$$sin^2\theta = \frac{\lambda^2}{4a^2}[(h^2+k^2+hk) + l^2\frac{a^2}{c^2}] \tag{3.3}$$

the lattice constant 'a' is calculated for (100) plane by using the expression 3.4 [65]:

$$a = \frac{\lambda}{\sqrt{3}.sin\theta} \tag{3.4}$$

The lattice constant "c" is calculated for (002) plane by using the expression 3.5 [65] :

$$c = \frac{\lambda}{sin\theta} \tag{3.5}$$

The calculated lattice parameters along with their ratio "c/a" are tabulated in Table 3.1

Crystallite size was obtained by Debye-Scherrer formula given by equation 3.6.

$$D = \frac{K\lambda}{\beta cos\theta} \tag{3.6}$$

Where D is the crystallite size, 0.94 is the particle shape factor which depends on the shape of the particles, λ is the CuK_α radiations (1.5405 Å), β is the full width at half maximum (FWHM) of the selected diffraction peak corresponding to <101> plane and θ is the Bragg angle obtained from 2θ value corresponding to maximum intensity peak in XRD pattern.

Volume of ZnO and ZnO-Cu unit cell "V" is determined by using the expression 3.7:

$$V = \frac{\sqrt{3}a^2c}{2} \tag{3.7}$$

TABLE 3.1 – Cristallite size and lattice parameters of Cu doped ZnO nanopowders with different Cu concentration.

Sample	2θ du pic (101)(°)	β (101) (°)	c (Å)	d_{101} (Å)	D (nm)	a (Å)	V ($Å^3$)
ZnO	36,251	0.264	5,222	2,473	31	3.246	47,59
ZnO:Cu (1%)	36,269	0.288	5,213	2,474	29	3,246	47,53
ZnO:Cu (3%)	36,353	0.24	5,202	2,474	34	3.241	47,16
ZnO:Cu (5%)	36,309	0.312	5,195	2,469	26	3.248	47,43
ZnO:Cu (7%)	36,297	0.192	5,204	2,469	43	3,240	47,28

From table 3.1, we observed that the lattice parameters "a" and "c" decreased with Cu doping concentration (x= 0.01 and x= 0.03) due to substitution of smaller Cu^{+2}

ions, replacing larger Zn^{+2} ions. Both the parameters increase slightly with higher doping concentrations (x= 0.05, 0.07), in accordance with Vegard's law .

It is observed in Table 3.1 that average crystallite size "D" decreased with the increase in dopant concentration. The decrease in the size of ZnO NPs through Cu-doping suggests lattice disorders owing to the strain induced as a consequence of doping (close ionic radii of Cu (0,73 Å) and Zn (0,74 Å). [68]

3.2 Fourier transform infrared (FTIR) studies

Figure 3.4 shows the FTIR spectrum of pure ZnO and Cu doped ZnO nanoparticles synthesized at 130°C by solvothermal method. The bands at 3676–3340 cm^{-1} correspond to the O–H mode vibration of H_2O in Cu–Zn–O/Zn-O lattice, and hydroxyl groups which may be due to moisture in the solution and the atmosphere. [69]
The strong asymmetric stretching mode of vibration of C=O from the COOH group was observed allmost 1406 , 1401 ,1403 cm^{-1} [70] [72], the medium to weak bands at 835 cm^{-1} and 624 cm^{-1} are assigned to the vibrational frequencies due to the change in the microstructural features by the addition of Cu into Zn–O lattice, the stretching mode of vibration corresponding to C=C is obtained at 1032 ;1038 ;1042 cm^{-1}.

The Zn–O bond is assigned to the stretching frequency at 566 cm1 for pure ZnO which is shifted to higher frequency as 567 cm^{-1} for Cu = 0.01, 574 cm^{-1} for Cu = 0.03, 571 cm^{-1} for Cu = 0.05 and 575 cm^{-1} for Cu = 0.07. [71]
Copper atom is slightly lighter than Zn atom, so, according to the well established theories of vibrational modes in mixed crystals the substitution should result in an upward shift of the fundamental transverse optical phonon mode.

3.3 Thermal analysis (TGA/DTGA/DTA)

In order to investigate the effect of doping concentration on thermal properties of pure and Cu-doped ZnO nanoparticles, thermogravimetric and differential thermal analysis(TG/DTA) are carried out.

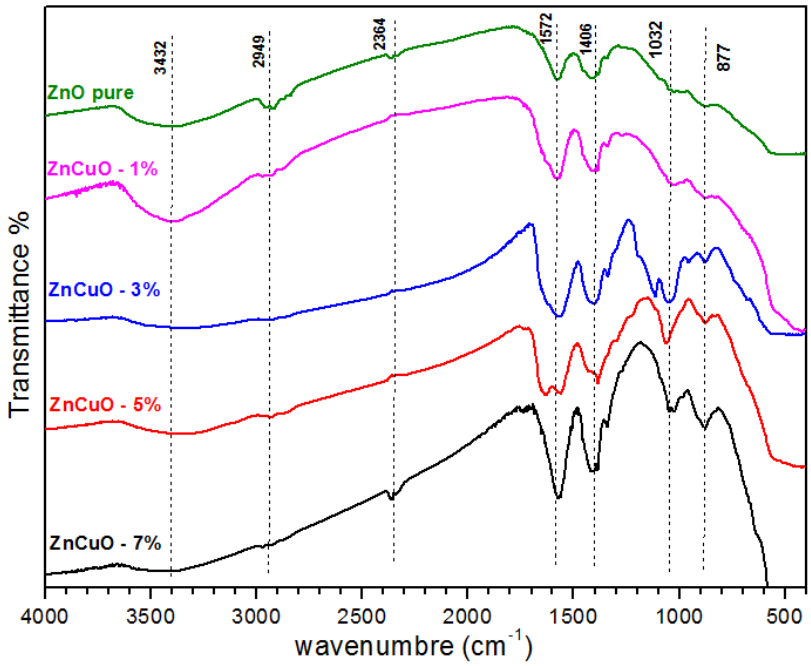

FIGURE 3.4 – FTIR spectre of pure ZnO and Cu doped ZnO nanoparticles.

3.3.1 Case of ZnO pure

Figure 3.5 shows the thermogravimetric curves (TG), its derivative (DTG) and the ATD of the powder synthesized by the solvothermal technique using ethanol as solvent, the powder was dried at 80 ° C for 2 Days.
Thermogravimetric analyzes were carried out with a temperature rise ramp rate from 20 ° C / min from ambient to 800 ° C. The TG curve shows four areas of loss of mass at temperatures below 180; 180-316; 320-525; 525-800.

Below 180: The first (0,27%) observed in the range temperature below 180 °C with an endothermic peak in the ATD curve at 113 ° C is due to evaporation of water on the surface of nanoparticles (ZnO2, xH2O → ZnO2) [73] and organic compounds (at TR-110 °C) and dehydroxylation of hydroxide precursor to oxide compound
from 180 to 320 : the second loss (1,985%) between 180 ° C and 320 ° C with an endothermic peak at 229 ° C and an exothermic peak at274 ° C

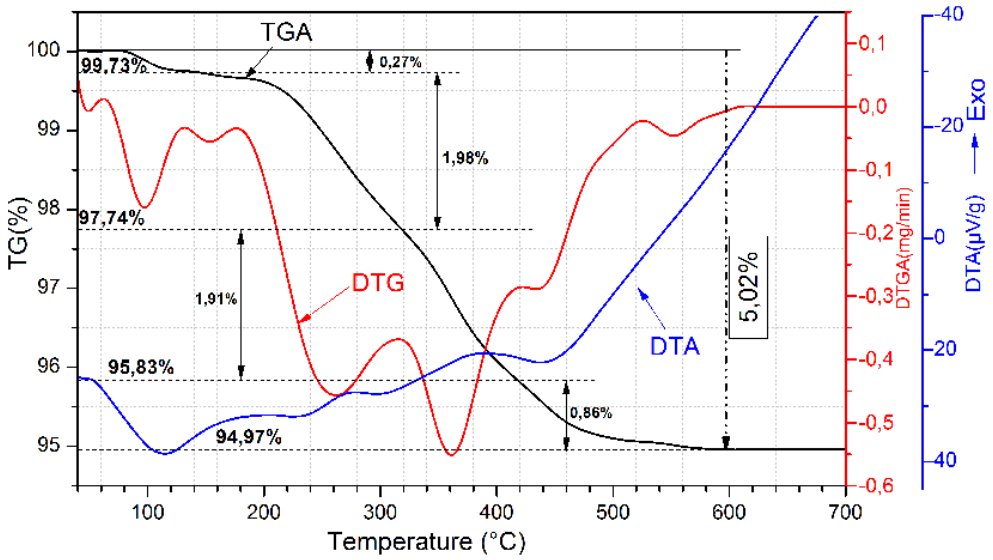

FIGURE 3.5 – DTA/TG and DTG curves of solvothermal ZnO nanoparticles.

From 320 to 419: the third mass loss (1,91%) of 316 ° C to 400 ° C with an exothermic peak at 380 ° C is ascribed to decomposition of nitrate group .
From 419 to 700: The fourth mass loss (0,86 %) with an endothermic peak at 440 ° C is attributed to complete decomposition of precursor to ZnO

The DTA curve showed endothermic and exothermic at 113 ° C, 229 ° C, 440 ° C and at 274 ° C, 380 ° C peaks. These peaks are attributed to the evaporation of water and the decomposition of hydroxide groups.

The endothermic peaks at 113 ° C, 229 ° C, 440 ° C. The first peak corresponds evaporation of water and ethanol, while the last two peaks are related to the decomposition of MEA (Monoethanolamine) and organic residues.

3.3.2 Case of ZnCuO (3% ; 5%)

Figures 3.6 shows the thermogravimetric curves (TG), its derivative (DTG) and (ATD) of ZnCuO nanoparticles synthesized by the solvothermal technique, were they dried at 80 ° C for 12 h. Thermogravimetric analyzes have been carried out with a temperature rise ramp rate of 20 ° C / min of the ambient temperature at 800 ° C.
The curves shown that the areas of loss of mass are allmost the same of Un-doped

ZnO which we find before.

In general, metal oxides such as ZnO and CuO/Cu2O have a high melting temperature, It is well known that ZnO is decomposes at temperatures above 1200 ° C under atmospheric pressure. (Tm of ZnO is 1975 ° C, Tm of CuO/Cu2O is 1326 / 1235 °C), and does therefore cannot be decomposed at low temperature.

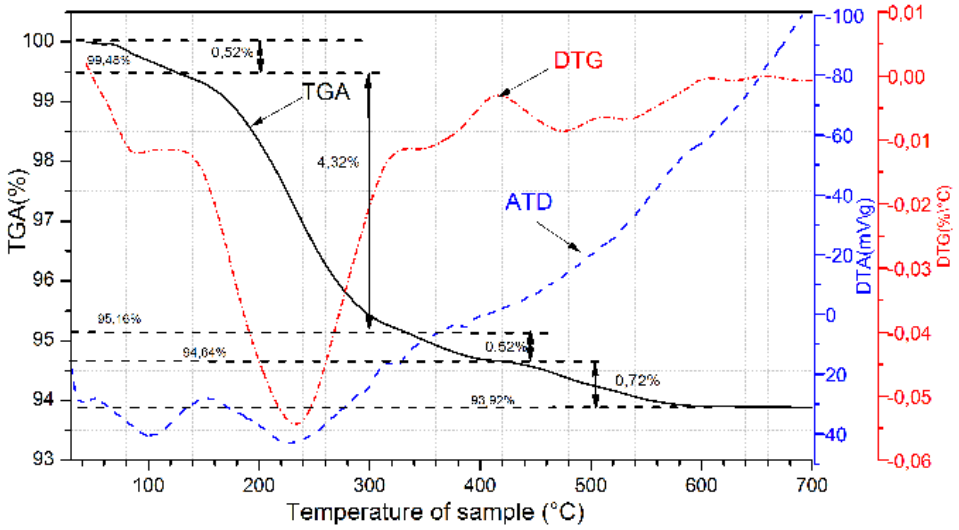

FIGURE 3.6 – DTA/TG and DTG curves of solvothermal Cu doped $Zn_{0.97}Cu_{0.03}O$ nanoparticles.

so that whay we didn't find any peaks or areas of loss of mass correspend to ZnO , CuO /Cu_2O

- The Comparison :

Comparison of Fig. 7(a) and (b) reveals that total weight loss of pure ZnO 5,05%) is greater than $Zn_{x-1}Cu_x$ O (x=0,005) (3,40 %) and $Zn_{x-1}Cu_x$ O (x=0,003) (3,45%) These results indicate that nanoparticles are pure Without any impurities

It shows that the phase transition decreases due to decrease in weight loss as a result of doping of 'Cu' in ZnO and the sample becomes more stable

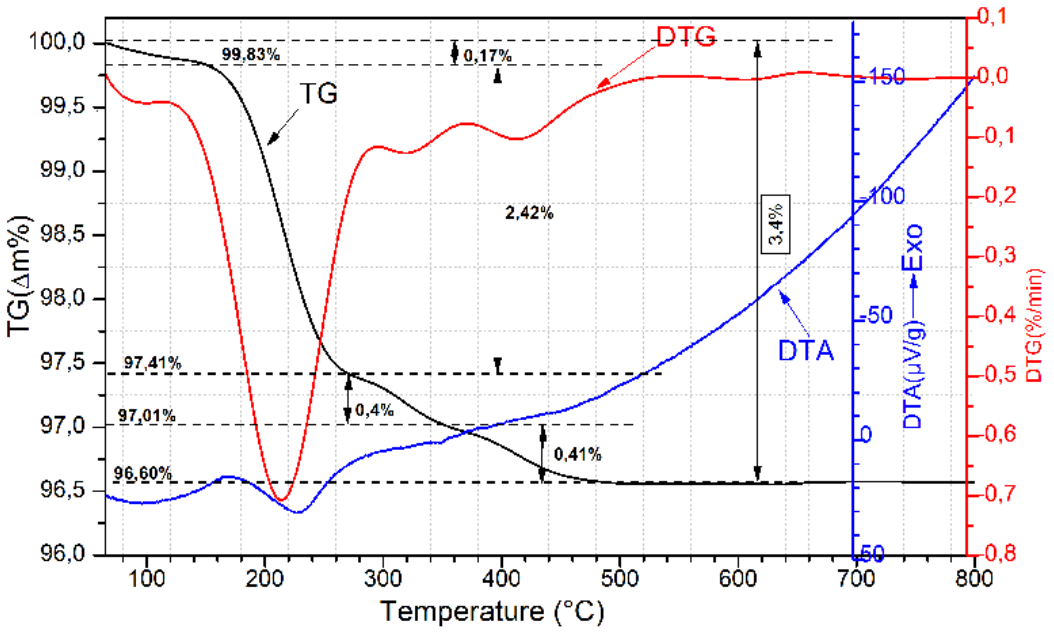

FIGURE 3.7 – DTA/TG and DTG curves of solvothermal Cu doped $Zn_{0.95}Cu_{0.05}O$ nanoparticles

Conclusion

The work presented in this dissertation focuses on the development and study of the properties of undoped and Copper-doped zinc oxide ($Zn_{1-x}Cu_xO$) nanoparticles, using the Solvothermal technique at 130°C and from the chemical reaction between the precursors acetate Zinc dihydrate, copper nitrate, the solvent of ethanol and the stabilizer monoethanolamine. We have interested in the study of the effect of doping on the properties of ZnO nanopwders. The synthesized nanopowders have been characterized by X-ray diffraction (XRD) for the study of structural, TG/ DTA thermagravimetry, FTIR spectroscopy .

- Structural studies has shown that synthesized powders crystallize in a hexagonal würtzite structure, wich mean that Cu incorporatation into crystal structure of ZnO, the calculation of the size of the crystallites showed that they are of a nanometric order, i.e. 30 and 25 nm for the NPs of ZnO/ZnCuO .

- The increases of lattice parameters "a" and "c" and volume of unit cell in ZnCuO indicate that Cu ions substitute in Zn site with increasing Cu concentration.

- The spectroscopic characterization by IR made it possible to reveal all the chemical bonds existing in the ZnO / ZnCuO nanopowders. It will be necessary to retain from these results confirm what was found by DRX, that is to say that our powders are solid solutions in which no new phase appears.

- The protocol followed in this dissertation work using the solvothermal route allows the development of nanoparticles of nanometric size with a good crystalline quality and high purity at very low temperature, without calcination.

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Abstract

Undoped and Cu doped ZnO nanoparticles ($Zn_{1-x}Cu_x$ O) with x = 0.0, 0.01, 0.03, 0.05 and 0.07 were prepared by Solvothermal method at 130°C. Structural and thermal properties of samples were investigated by X-ray diffraction (XRD), thermogravimetric, differential thermal analysis (TG/DTA) and FTIR spectroscopy. XRD analysis confirms that all samples have hexagonal structure with no impurity phases, which suggest that Cu ion successfully incorporated into the ZnO crystal structure. The lattice parameters, volume of unit cell,and cristallite size were calculated from XRD pattern of samples, and it was found that the average cristallite size was in the range of 26 nm to 46 nm. The TG and DTA measurements gave us information about the thermal transitions. The TG and DTA measurements confirmed the purity of the synthesized ZnO / ZnCuO nanopowders, and showed that the loss of mass, which corresponds to the various endothermic and exothermic peaks, corresponds to the evaporation of water, alcohols, groups of nitrate, acetate and Monoethanolamine. The functional group and chemical interactions of ($Zn_{1-x}Cu_x$ O) samples were also determined at various peaks using FTIR data.

Keywords : $Zn_{1-x}Cu_x$ O , Solvothermal, FTIR, TG/DTA, XRD, Nanoparticles

الملخص

تم تحضير الجسيمات النانوية لنظام $Zn_{1-x}Cu_xO$ بتركيزات 0.0 و 0.01 و 0.03 و 0.05 و0.07 بطريقة المذيب الحراري عند 130C ° درجة مئوية. تم فحص الخواص الهيكلية والمفورولوجية للبلورات النامية باستخدام تقنية حيود الأشعة السينية (DRX) والتحليل الحراري التفاضلي والقياس الحراري (TG / DTA) والتحليل الطيفي FTIR على التوالي. يؤكد تحليل DRX أن جميع العينات لها بنية سداسية بدون شوائب مما يشير إلى أن أيون النحاس قد تم دمجه بنجاح في الهيكل البلوري ZnO بنية بلورية سداسية . تم حساب المعلمات الشبكية ، وحجم خلية الوحدة ، وحجم الحبوب من نمط DRX لعينات ZnO النقية وعينات النحاس المخدر ووجد أن حجم الحبوب كان في حدود26 نانومتر إلى 46 نانومتر. أعطتنا قياسات DTA معلومات حول التحولات الحرارية. أكدت قياسات TGA و .DTA نقاء المساحيق النانوية المصنعة من ZnO / ZnCuO ، وأظهرت أن فقدان الكتلة الذي يتوافق مع مختلف القمم الماصة للحرارة والطاردة للحرارة ، يتوافق لتبخر الماء والكحولات ومجموعات النترات والأسيتات والمونويثانولامين. تم تحديد المجموعة الوظيفية والتفاعلات الكيميائية لعينات $Zn_{1-x}Cu_xO$ أيضًا في قمم مختلفة باستخدام بيانات FTIR .

الكلمات المفتاحية :

طريقة المذيب الحراري ، FTIR, TG/DTA, DRX, جسيمات نانوية, ($Zn_{1-x}Cu_xO$)