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Study of Structural and Optical Properties of Crystals Grown by Solution Growth Technique

A Thesis

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دراسة الخصائص التركيبة والبصرية لبلورات منماة بتقنية الانماء من المحلول





اشراف

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Dedication

I dedicate this effort TO My Father, My Mother, My Brothers, My Sisters and My Friends With all my gratitude

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Abstract

Single crystals of copper sulfate pentahydrate (CSP) were grown from aqueous solution in three batches by slow evaporation technique at room temperature. The first batch included grown crystals by using double distilled water as a solvent with (0.25 M, 0.5 M, 1 M, 1.5 M, 1.5 M-59 °C, 2 M-27 °C, 2 M- 50 °C and 2.5- 40 °C M). The obtained crystals $[(39 \times 12 \times 3), (33.05 \times 30.5 \times 4.7),$ (21.6×19.38×3), dimensions were (19.12×15.3×5.5), (25.6×21.36×7), (11.5×15×4), (15.56×20.14×6.78), $(23.8 \times 20.3 \times 5.54)$] mm³ respectively. The second batch included study the influence of H₂SO₄ acid on grown crystals with (0.2 M, 0.4 M, 0.6 M, 0.8 M and 1 M). The obtained crystals dimensions were $[(34.7 \times 20.3 \times 6.54)]$, (50.68×23.4×8.3), (17.4×37.6×6.7), (24.14×15×7.7), (14.5×34.11×42.3)] mm³ respectively. It was found that the growth rate of all faces of crystals were decreased with reducing molarity of (CSP) solution. The third batch included the study of the influence of magnetic water on grown crystals with (0.25 M, 0.5 M, 1 M, 1.5 M and 2 M). The obtained crystals were with dimensions of $[(20.9 \times 18 \times 2.7), (18.1 \times 16.3 \times 3.6), (42.4 \times 27.36 \times 7.5),$ $(27.68 \times 23.74 \times 9.1)$, $(20 \times 9 \times 7.1)$] mm³ respectively. It was found that the magnetic water did not improve the morphology of (CSP) crystals. Structure analysis of grown crystals from three batches were carried out by X-ray diffraction technique. XRD measurements showed that the crystal system was triclinic and the lattice parameters were in agreement with the (ICDD) cards. The study of the vibrational mods for the grown crystals was conducted by FTIR spectroscopy. It was found that the H₂SO₄ acid and magnetic water leads to decrease the intensity of transmittance compared to the distilled water, and it was observed that the metal ion Cu⁺² Cu-O-H appear in the crystals was grown by using distilled water and did not appear in the crystals grown by using H₂SO₄

acid and the appearance was with less intensity in the crystal from magnetic water. The UV-Visible spectra were studied to identify the transmission and to calculation absorption coefficient and energy gap, and it was found that the H₂SO₄ acid causes to decrease of the transmittance, and it is noted that the magnetic water causes the decrease in the transmittance but by lower rate. Also, it was found that the increase molarity leads to increase the transmittance of spectrum of crystals grown using distilled water and magnetic water as a solvent. Also, it was found that the decrease of molarity leads to increase the transmittance of spectrum of crystals grown by using H_2SO_4 acid as a solvent. It was found that the absorption coefficient of crystals grown used distilled water and magnetic water decreases by increasing the molarity. It was noted that it increases by increasing the molarity for crystals grown used H₂SO₄ acid. Also, it was found that the acid leads to increase the absorption coefficient compared to the crystals grown from distilled water and magnetic water. It was observed that the energy gap increases by increasing the molarity at the crystals grown used distilled water and magnetic water as a solvent, but it was decreased by increasing the molarity at crystals grown using acid as a solvent. The energy gap decreases in the crystals grown using acid H₂SO₄ as a solvent about the crystals grown using distilled water and magnetic water as a solvent. The polarizing microscope analysis shows that the CSP crystal loses all water molecules at the temperature (150 $^{\circ}$ C).



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List of Symbols

F

and abbreviations

Symbols	Meaning
TGA	Dynamic and isothermal
CSP	Copper sulfate pentahydrate
СМС	Critical micellar concentration
FTIR	Fourier Transform Infrared
UV	Ultra Violet
ΔG	Total free energy (J)
ΔG_s	Free energy per unit surface (J)
ΔG_v	Free energy per unit volume (J)
γ	The surface energy or interfacial tension
r _c	Critical nucleus (Å)
J	The rate of nucleation
D	Pre-exponential constant
K _B	Boltzmann constant (J/K)
T _c	Absolute temperature (K)
С	Concentration of solution
C*	Equilibrium saturation
V	The molecular volume
Δμ	The driving force (J)
$\mu_{\rm m}$	Chemical potential of solution phase (J)
μ _c	Chemical potential of crystal phase (J)
S	The supersaturation ratio
n _i	The number of <i>i</i> th ions in the molecule of the crystal
a_i , $a_{i,e}$	Actual and equilibrium activities of the <i>i</i> molecule in the crystal
hkl	Miller Indices

d _{hkl}	Interplanner Spacing (Å)
n	The positive integer and it is order of the reflection
λ	The wavelength (nm)
θ	Diffraction angle (degree)
λ_c	The cut off wavelength (nm)
Eg	Energy Band gap (eV)
I _A	Absorbed light intensity (mW/cm ²)
Io	Incident intensity of light (mW/cm ²)
I _T	Intensity of transmitting light (mW/cm ²)
А	Absorbance
Т	Transmittance
t	Thickness of the sample
hu	Photon energy
α	Absorption coefficient
В	The inversely proportional to amorphousity
SG	Specific gravity
$\rho_{H_2SO_4},\rho_{H_2O}$	Density of sulfuric acid and water respectively (m/v)
М	Molar concentration
M _{wt}	Molecular weight (g/mol)
W _t	Weight (g)
XRD	X-Ray Diffraction
PXRD	Powder X-Ray Diffraction
R. T.	Room temperature
PM	Polarizing microscope
TGS	Triglycine sulfate



1-1 Introduction

This chapter gives a general introduction to the topic contained in the thesis. This part deals with the general concepts regarding to the growth of single crystals.

1-2 A brief history of crystal growth

Crystals are the unrecognized pillars of the modern technology [1]. Although crystals have intrigued mankind since ancient times owing to their beauty and rarity, crystallography as an independent branch of science essential aspects had been derived from early crystallization experiment in the eighteenth and nineteenth centuries [2]. Theoretical understanding started with the development of thermodynamics in the late 19th century and with the development of nucleation and crystal growth theories and the increasing understanding of the role of transport phenomena in the 20th century [3].

The science of crystals -Crystallography- has undergone many changes in the course of its development [2]. Crystal growth is an important field of materials science, involving the controlled phase transformation [4]. A crystal is a solid limited by plane surfaces where the atoms or molecules in the crystal are arranged orderly in a space lattice with particular geometrical symmetry [4,5].

Without crystals, there would be no electronic industry, photonic industry, fiber optic communications. All depend on materials/crystals such as semiconductors, superconductors, polarizers, transducers, radiation detectors, ultrasonic amplifiers, ferrites, magnetic garnets, solid state lasers, non-linear optics, piezo-electric, electro-optic, acousto-optic, photosensitive, refractory of different grades, crystalline films for microelectronics and computer industries [6].

Crystal growth is a highly interdisciplinary subject that demands the collaboration of physicists, chemists, biologists, engineers, crystallographers, process engineers, materials scientists, and materials engineers [7]. More recently, crystals of scientific and technological importance such as semiconductors or laser materials have received the greatest attention and have formed the basis of new industries [8].

The world crystal production is estimated at more than 20 000 tons per year, of which the largest fraction of about 60% are semiconductors silicon, GaAs, InP, GaP, CdTe and their alloys. As it can be seen in Figure (1.1), optical crystals, scintillator crystals, and acousto-optic crystals have about equal shares of 10%, whereas laser and nonlinear-optic crystals and crystals for jewelry and watch industry have shares of a few % only [3].



Fig. (1.1): Estimated shares of world crystal production in 1999 [3].

1-3 Single crystals

A single crystal is defined by long-range atomic order extending over many atomic diameters, and having a repetitive structure. As a result,

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crystals have rigidity, fixed shape, and mechanical strength [9]. The growth of a single crystal is the result of complicated interactions of physical phenomena [10].

The advantage of single crystals compared with polycrystalline is the absence of grain boundaries and often with less impurities. Physical properties of single crystals are anisotropic in nature and depend on the crystallographic orientation [11].

Most of single crystals, have distinguished optical, electrical, or magnetic properties, which make from single crystals, major elements in most of technical modern devices, as they may be used as lenses, prisms, or gratings in optical devices, or filters in X-Ray and spectrographic devices, or conductors and semiconductors in electronic, and computer industries. Furthermore, single crystals are used in transducer devices. Moreover, they are necessary elements in laser and maser emission technology [12]. Single crystals are utilized in such diverse applications infrared pharmaceuticals, computers, detectors, frequency as measurements, piezoelectric devices, a variety of high-technology devices, and sensors [4].

1-4 Classification of crystal growth

Crystal growth is a heterogeneous or homogeneous chemical process involving solid or liquid or gas, individually or together, to form a homogeneous solid substance having three-dimensional atomic arrangement [7]. The techniques of growing crystals are very wide and mainly dictated by the characteristics of the material and its size. The free energy of the growing crystal must be lower than starting phase of the system. It is the common condition for all crystal growth processes [13]. The method of crystal growth may range from a small inexpensive technique to a complex advanced expensive process, and crystallization time ranges from minutes to months [14]. Almost all methods of crystal growth involve preparation of a solid phase. The methods of crystal growth can be classified into three main categories [4]:

- i. Solid growth (solid \rightarrow solid)
- ii. Vapour growth (vapour \rightarrow solid)
- iii. Liquid growth (liquid \rightarrow solid)

The classification of crystal growth technique is shown in figure (1.2).

1-5 Crystal growth techniques from solutions

Growth from solutions is the most common and the oldest technique of crystal growing compared with vapor-phase melt growth and it occupies an outstanding position due to its versatility and simplicity. Growth from solutions falls into the category of polycomponent growth techniques. Here, there will be at least two components - namely, the solvent - most commonly water - and the solute that are solid in their pure [7,14,15,16].

Solution growth is used for materials, which have high solubility and have variation in solubility with temperature [7,15]. The important advantage of solution growth is the control that it provides over the growth temperature, simplicity of equipment, control of solubility by varying the solution temperature and the high degree of crystal perfection since the crystals grow at temperatures just below their melting point [7,14]. The equipment is relatively simple, the crystals exhibit a high degree of perfection, and the conditions of growth-temperature, composition of the medium, types of impurities can be widely varied [15]. The crystal growth from method of solution falls into the following[7]:



Fig. (1.2): Scheme of crystal growth technique [7].

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- i. Slow evaporation.
- ii. Slow cooling.
- iii. Temperature gradient.

The present work involves the growth of single crystals from slow evaporation process at room temperatures.

1-6 Slow evaporation method

This is the oldest and simplest method of crystal growth, and it is the best method to grow crystals by solution technique. The temperature is fixed and the provision is made for evaporation. With nontoxic solvents such as water, it is permissible to allow evaporation into the atmosphere. Typical growth conditions involve temperature stabilization to about \pm 0.005 °C and rates of evaporation of a few mm³/hr. In this method, an excess of a given solute is established by utilizing the difference between the rates of evaporation of the solvent and the solute. In contrast to the cooling method, in which the total mass of the system remains constant, in solvent evaporation method, the solution loses particles, which are weakly bound to other components and the volume of the solution is higher than the vapour pressure of the solute and the solvent evaporates more rapidly and the solution becomes supersaturated .

The advantage of using this technique is that the crystals grow be at constant temperature. This technique can effectively be used for materials having very low temperature coefficient of solubility. But inadequacies of the temperature control system still have a major effect on the growth rate [17,4].

1-7 Applications of copper sulfate pentahydrate crystal

The copper sulfate pentahydrate crystal can applied as broadband UV optical filters because of its spectral characteristics of chalcanthite crystal [18].

1-8 Previous studies

In (1964), Gruzensky [19] grew crystals of CuSO₄ from a non-aqueous solvent of $(NH_4)_2SO_4$ and H_2SO_4 . Solubility of CuSO₄ in solvents of varying $(NH_4)_2SO_4$ to H_2SO_4 ratio, at 200 °C has been determined, as the solubility of CuSO₄ in pure H_2SO_4 is relatively low, but it increases rapidly as the $(NH_4)_2SO_4$ content of the solvent increases. The temperature dependence of the solubility in 0.35 $(NH_4)_2SO_4 - 0.65 H_2SO_4$. In three or four days, single crystal weighing up to 150 mg have been obtained.

In (1974), Chasen [20] studied the habit and orientation in growth solution of crystal of copper sulfate pentahydrate. The crystal growth was done by refrigeration method.

In (1976), Berger [21] grew single crystals of CuSO₄.5H₂O and CuSeO₄.5H₂O by slow evaporation process at (18 °C) of an aqueous solution with some sulfuric acid added. The sizes of a single crystal CuSO₄.5D₂O obtained were of 1 or 2 cm³. Infrared and Raman spectra were studied for CuSO₄.5H₂O and CuSeO₄.5H₂O. It was found that the sulfate ions are more strongly perturbed by the hydrogen bonds to the D₂O molecules in the crystals of CuSO₄.5D₂O.

In (1979) Nandi et al. [22] employed slow evaporation process to grow single crystal and polycrystalline of copper sulfate pentahydrate. It has been observed that the dehydration of crystal takes place in the steps of 1

7

mol, 1 mol, 2 mols and 1 mol at temperatures 111, 124, 190 and 275 C respectively in one of the sets. The electrical conductivity (DC), dielectric constant (at 10 kHz), dynamic and isothermal TGA were studies. The DC electrical conductivity and dielectric constant also show a large increase and decline near about the first two dehydration temperatures confirming the results of TGA study.

In (1989), Zumstein and Rousseau [23] found different growth kinetics of small and large crystals of copper sulfate pentahydrate. Small crystals generated by the contact nucleation had a distribution of invariant growth rates which caused an increase in the variance of the crystal size distribution as the population was allowed to grow. Random growth rate fluctuations were found to be insignificant. The growth rates of all small crystals had the same dependency on supersaturation, which means that the effects of growth rate dispersion were independent of supersaturation. Large crystals grew at much faster rates than the contact nuclei under similar supersaturations.

In (1996), Giulietti et al. [24] studied changes in habit of copper sulfate pentahydrate crystal during cooling crystallization experiments in the temperature range of 70 to 30 °C. A slow linear cooling rate (batch time of 90 min) predominantly caused the appearance of well-formed crystals. Exponential cooling (120 min) resulted in the additional formation of agglomerates and twins.

In (1999), Giulietti et al. [25] studied different batch cooling modes of copper sulfate pentahydrate aqueous solutions to find best conditions for the investigation of the effect of additives on crystallization. Three types of additives (solvents, ionic substances and surfactants) had been used and their effect on crystal size, habit and yield was studied. Crystals

produced in the absence of additives are predominantly flat with dominant faces |1 -1 0| and |1 1 0|, sometimes |1 0 0| and |0 0 1|. Ethanol slightly reduces the face |1 - 1 0| and the face |1 0 0| is slightly prolonged, but the shape is in principle unchanged. Other solvents (n-butylalcohol and acetone) as well as H^+ and Zn^{2+} did not affect the CSP crystal habit significantly. Small amount of Fe³⁺ induced the formation of nearly prismatic crystals; the growth rate of the |0 0 1| and |1 1 0| faces seems to be significantly reduced so that the overall growth rate is decreased and this result also in lower yield (immediately at the end of cooling, so that a significant mass of CS remained in the solution). The overall growth rate of CSP is significantly reduced by Fe³⁺ and detergents, whereas the nucleation rate is increased by these additives. The kinetic exponent of crystallization n/g of pure CSP is within expected limits and is markedly reduced in the presence of Fe^{3+} . The value of the system constant of crystallization B_N decreases with the addition of ethanol and in particular in presence of Fe^{3+} .

In (1999), Freitas et al. [26] studied the influence of magnetic field on kinetic crystallization parameters of zinc sulfate-water and copper sulfate-water systems were investigated in a series of controlled batch cooling experiments. The solutions were exposed to magnetic fields with different intensities, up to a maximum of 0.7 T. A clear influence of magnetic field on the zinc sulfate crystallization parameters was found: an increase in the saturation temperature, a decrease in the metastable zone width, and increased growth rate and average crystal size. The magnetic effect ("magnetic memory") remained in the solution for at least 150 min after the magnetic exposure. These effects were observed for the diamagnetic zinc sulfate, but not in similar experiments with paramagnetic copper sulfate.

In (2002), Vijayan et al. [27] used slow evaporation solution growth technique to grow semicarbazone of benzophenone single crystals. The X-ray diffraction analysis revealed that the crystal belongs to the triclinic crystal system and space group P1. From FT-IR studies it was found that the compound possesses both free and hydrogen bonded N–H stretching modes. The hydrogen bonded N-H stretching mode was found to be the major driving force for packing of molecules in the crystals. The transparency of the grown crystals had been confirmed using UV-Vis spectra. **UV-Vis** spectra revealed that the semicarbazone of benzophenone is highly transparent between the wavelengths 400 to 800 nm.

In (2004), Mericcan [28] grew (CuSO₄.5H₂O) ionic crystal under room conditions by using slow cooling and slow evaporation solution growth technique. The cooling at room temperature for the system at 70 °C produced a thick layer of randomly scattered tiny crystals, near to an amorphous structure. The layer produced was opaque and the amount of precipitate produced was at maximum. Unexpectedly, a layer showing the melting of ice could be observed; the system had drawn ice from the refrigerator. The cooling at 0 °C for the system at 70 °C produced crystals were a bit "proper", with a scattered combination of layers of larger crystals and containing some translucency. The amount of precipitate produced was less than system cooling at room temperature. The system at 40 °C produced crystals, with a thinner layer of precipitate, were completely translucent. The system produced interconnected, but distinguishable layer of crystals, with larger and more discrete ones on the top. The system at room temperature produced distinguishable large crystals, intact in shape. It was noticed that the rate of evaporation of a

saturated solution of copper (II) sulfate pentahydrate in room temperature had a significant effect on intact crystal growth.

In (2006), Vijayan et al. [29] grew L-Alanine single crystal by slow evaporation solution growth technique at room temperature. Good transparent single crystals (size $1.7 \times 0.8 \text{ cm}^2$) were obtained after two weeks. The grown single crystal had been subjected to powder X-ray diffraction analysis and it was confirmed that the grown crystal belongs to the orthorhombic crystal system. The crystalline perfection was evaluated by high-resolution X-ray diffraction analysis (HRXRD). The functional groups of the grown crystal had been confirmed by FTIR and Raman spectra analyses. It was concluded that the hydrogen bonding due to NH_3^+ and COO⁻ moieties is the additional major force in the crystal lattice. The number of protons present in the compound was confirmed by FT-NMR analysis. The optical behavior was analyzed by UV-Vis measurement and it was observed that the minimum absorption was in the visible region.

In (2008), Fei Lu et al. [30] had succeeded in preparing $CuSO_4.5H_2O$ crystals with different orientations and morphologies by using Langmuir– Blodgett films of stearic acid as templates. The experimental results demonstrated that the Langmuir–Blodgett film in the liquid state have the ability of directing the nucleation and growth of crystals. X-ray diffraction patterns of the prepared crystals showed that the orientation of the attached crystals on the Langmuir–Blodgett film is affected by temperature greatly. The morphologies of the crystals showed that the shapes and colors of $CuSO_4.5H_2O$ crystals affected strongly on orientation changes. In (2009), Naware and Kelkar [31] prepared mixed single crystal made by mixing saturated aqueous solutions of NiSO₄. $6H_2O$ and CuSO₄. $5H_2O$ and using slow evaporation method. The crystals were characterized by UV-Visible, FTIR and single crystal X-ray diffraction studies. The UV-Visible spectrum was recorded and it was observed that absorption maxima of mixed single crystal obtained in between the range of pure salts. From FTIR spectra shows some new bands and some shifts in peaks for mixed single crystal. XRD suggests tetragonal crystal structure.

In (2013), Singh et al. [32] studied the effect of ionic surfactants, alcohols and batch cooling on the morphology of copper sulfate pentahydrate. It was found that nonionic surfactants have a marginal effect on this ionic compound, whereas ionic surfactants were able to modify the morphology substantially. Alcoholic antisolvents were also found to be effective habit modifiers that produce elongated crystals. It was shown that the effects of surfactants and antisolvents can be combined by using a surfactant–antisolvent pair. The effect of surfactant was observed after a certain threshold concentration. A detailed study of the critical micellar concentration (CMC) of sodium dodecyl sulfate in copper sulfate pentahydrate solution confirmed that this threshold concentration is close to the CMC of the surfactant in copper sulfate pentahydrate solution. Evidence suggested that a concentration higher than CMC was required to maintain a surfactant reservoir in the system, leading to a change in the crystal morphology.

In (2013), Manimekalai and Raja [33] employed slow solvent evaporation method at 300 K to grow Ethylene Diamine Tetra Acetic acid doped copper sulfate pentahydrate for five different parent-dopant combinations. The X-ray diffraction analysis reveals the quality and purity of the grown crystal. The modes of vibrations of different molecular groups present in
grown crystal were identified and the complex formation with copper was confirmed by FTIR technique. The UV-Visible spectrum reveals that the grown crystals are transparent in the wavelength region 200-1100 nm. The lower cut off wavelength was ~190 nm.

In (2013), Manomenova et al. [18] had grown large single crystals of optical quality of copper sulfate pentahydrate (CSP) by used the seed of (CSP) crystals ($5 \times 5 \times 3$) mm³ in size, which formed as a result of spontaneous crystallization upon cooling supersaturated solutions to room temperature. Large (CSP) single crystals (up to $120 \times 65 \times 25$ mm in size) were grown. They can be applied as broadband UV optical filters. Their transmission spectra are measured the transmission band in the range of (280-570 nm). The temperature of dehydration is determined to be 46 °C. The internal crystal homogeneity was estimated by X-ray topography.

In (2014), Delphine et al. [34] have grown single crystals of pure and Lhistidine doped Copper sulfate by slow evaporation of an aqueous solution at room temperature. Powder X-ray diffraction analysis were studied to discover the crystalline nature. UV-Visible spectra have been recorded in the range 190-1100 nm.

In (2015), Anne et al. [35] employed slow evaporation method at room temperature to grow single crystals of pure and L-histidine doped copper sulfate pentahydrate. The grown crystals were studied by powder X-ray diffraction investigation to discover the crystalline nature. UV-visible spectra of pure and the L–Histidine doped copper sulfate crystals were recorded and it is found that the absorbance is less than one unit in the entire visible region. The transmission band in the range of 320-600 nm. The band gap value of copper sulfate crystal was found to be 4.08 eV.

The vibrational modes of functional groups were identified using FTIR spectroscopic technique.

1-9 Objectives of this study

This study aims to:

- 1. Growing single crystals of copper sulfate pentahydrate from aqueous solution by using slow evaporation technique at room temperature.
- 2. Studying the influence of solvents (distilled water, magnetic water and H_2SO_4 acid) on growth crystals.
- 3. Study of structural and optical properties of the grown crystals.

1-10 Steps of the Present Work

- ✓ Growth of copper sulfate pentahydrate (CSP) single crystal using distilled water as a water.
- ✓ Growth of copper sulfate pentahydrate (CSP) single crystal using aqueous solution of cupric acid (H₂SO₄) as a solvent.
- ✓ Growth of copper sulfate pentahydrate (CSP) single crystal using magnetic water as a solvent.
- ✓ powder and single crystal x-ray diffraction analysis to study structural properties of the crystals.
- ✓ Recording the Fourier Transform Infrared (FTIR) spectrum to find the functional groups and the modes of vibrations of different molecular groups present in grown crystal.

- ✓ Recording UV-Visible spectrum of polished single crystals to study transmission spectra, absorption coefficient and calculation energy gap.
- Polarizing microscope result analysis to know at what temperature CSP crystal is losing water molecules.



2-1 Introduction

This chapter includes the fundamental theories and the physical concepts of single crystals growth process.

2-2 Crystallization and precipitation kinetics

Crystallization process is a phenomenon of periodic arrangement of the constituent molecules of a given material obtaining a crystalline state [36]. It is a process of two-step. First step is nucleation which determines the initial formation of crystal, and the second step is crystal growth which determines their subsequent size. These steps require a change of free energy as shown in figure (2.1) [37]. Both steps, nucleation and crystal growth are equally important to the crystallization process [36].



Fig. (2.1): Schematic representation of crystallization [37].

The structural simplicity, purity and symmetry of crystal are responsible of the beauty of crystal. These characteristics provide the crystals with unique physical and chemical properties which caused major transformation in the electronics industry [38].

2-3 Nucleation and crystal growth

Crystal nucleation is an important phenomenon in crystal growth and it is a relatively rapid that it can occur in a matter of seconds. Nucleation is a key factor in controlling many properties of the appearance crystalline phase [16,39]. The ability to control this preliminary stage of crystal growth allows control of polymorphism and the size and distribution of crystals [40].

Nucleation is a process of birth of a new crystalline entity within a supersaturated solution [16,40], and it is the first formed embryos of the solid phase, which subsequently grow to produce perceptible crystal [3]. An embryo may grow or decay and disappear completely. In a supersaturated system when a few atoms or molecules associate together, a change in energy takes place in the process of formation of the cluster. This cluster is also known as a critical nuclei or nucleus. Nucleation in the kinetic theory is treated as the chain reaction of monomolecular added to the cluster and at last reaching macroscopic dimensions [14,41]. The critical cluster is formed by the collide of two monomers (molecule) with one another to from a dimer (molecular complex). Then the addition of a number of molecules (A) with a dimer to from a trimer, happens according to the following scheme [13,40]:

$$A_{(monomer)} + A_{(monomer)} = A_{2(dimer)},$$

$$A_2 + A = A_{3 (trimer)}, \dots, A_{n-1} + A = A_{n (cluster)}$$

The formation of the nucleus is a complex process and a difficult one, because the constituent atoms or molecules have to be oriented into a fixed lattice [13]. There are four stages involved in the formation of stable nucleus [37,13,40,42]:

- 1- Development of supersaturation: This may be attained due to changes in temperature, pressure, chemical reaction or any other physical or chemical condition.
- 2- Generation of embryo: The formation of embryo may be either homogeneous or heterogeneous.
- 3- Growth of the embryo from the unstable critical state to stable state.
- 4- Relaxation process, where the structure of the new born nucleus changes.

Nucleation is divided into two distinct types, primary and secondary nucleation, further the primary nucleation is divided into homogeneous and heterogeneous nucleation. This is shown in figure (2.2):

Homogeneous nucleation is a process that determined by the formation of stable nuclei or the spontaneous formation of crystalline nuclei within the interior of parent phase and this resulting from the absence of crystal or foreign in crystallization media. In contrast, heterogeneous nucleation is induced by the presence of foreign particles or surfaces present in the solution which can encourage the formation of nuclei at lower supersaturations levels [37,43,41]. The difference between the two mechanisms is shown in the figure (2.3).

The secondary nucleation is a mechanism of formation of new crystals from the presence of the crystals, also known as 'seeds', of the same substance and that mechanism is more favourable than both homogeneous and heterogeneous nucleation and thus it occurs at lower supersaturation [44].



Fig. (2.2): Types of nucleation [37].



Fig. (2.3): The difference between homogeneous and heterogeneous nucleation [45].

After the nuclei happened, it begins to grow. The crystal growth is the series of processes of layer by layer on surface by which an atom or a molecule is incorporated into the surface of a crystal, causing an increase in size. These different processes can be summarized into four steps: [16,41]

- 1. Transportation of atoms through solution.
- 2. Attachment of atoms to the surface.
- 3. Movement of atoms on the surface.
- 4. Attachment of atoms to edges and kinks.

In general, any crystallization process takes place by three basic steps achievement of supersaturation, formation of crystal nuclei and growth of these nuclei into crystals [14].

2-4 Crystal surface structure

Crystal growth theories are based on the considerations of the crystal surface structure [41]. On an atomic scale the growth surface of a crystal is irregular. It contains many kinks, free vacancies and unfinished atomic layers which may be used by atoms joining the crystal surface [46]. One of the most commonly used models was that provided by Kossel. This model envisions the crystal surface as made of cubic units which form layers of monoatomic height, limited by steps (or edges) as shown in figure (2.4). These steps contain a number of kinks along their length. According to this model, growth units attached to the surface will form one bond, whereas those attached to the steps and kinks will form two and three bonds, respectively. Hence, kink sites will offer the most stable configuration. Growth will then proceed by the attachment of growth units to kink sites in steps [41].

The kink will move along the step producing a net advancement of the step until this step reaches the face edge. Then, a new step will be formed by the nucleation of an island of monolayer height (or two-dimensional nucleus) on the crystal surface. This growth mechanism is normally referred to as single nucleation growth or layer growth and is represented in figure (2.5). A variation of this growth mechanism occurs when the nucleation rate is faster than the time required for the step to cover the whole crystal surface. In this case, 2D nuclei will be formed all over the surface and on top of other nuclei. These nuclei will spread and coalesce forming layers. This growth mechanism is normally referred to as multinucleation multilayer growth or birth and spread [41].



Fig. (2.4): Kossel model of a crystal surface [41].



Fig (2.5): Schematic representation of layer growth [41].

2-5 Energy formation of spherical nucleus

The total free energy change is associated with the process of formation of homogenous nucleation, ΔG is an overall excess free energy of the embryo between the two phases, ΔG_s is a positive quantity and it is proportional to r². r the radius of the nucleus. ΔG_v is a negative quantity, it is proportional to r³. This given as: [13,42]

$$\Delta G = \Delta G_s + \Delta G_v \qquad \dots \dots \dots (2-1)$$
$$\Delta G = 4\pi r^2 \gamma + 4/3\pi r^3 \Delta G_v \qquad \dots \dots \dots \dots (2-2)$$

 γ : The surface energy or interfacial tension.

 ΔG_v : Free energy per unit volume.

The quantities (ΔG , ΔG_s and ΔG_v) are shown in the figure (2.6)



Fig. (2.6): Change in free energy due to the formation of nucleus [47].

The total free energy change increases with the increase of the size of nucleus because the free energy of surface increases with r^2 and the free energy of volume decreases with r^3 [13]. The free energy ΔG of formation passes through a maximum ΔG_{crit} corresponds to critical nucleus r_c . For a spherical cluster, it is obtained by setting $d\Delta G/dr$ equal to zero : [42]

From equation (2-2) and (2-4) we get :

$$\Delta G_{\rm crit} = \frac{16\pi\gamma^3}{3(\Delta G_{\rm v})^2} = \frac{4\pi\gamma r_{\rm c}^2}{3} \qquad(2-5)$$

The behavior of a newly crystalline lattice structure in a supersaturated solution depends on its size, the crystal may grow or redissolve and it undergoes a decrease in the free energy of the particle. Particles smaller than r_c will dissolve if it presents in a liquid in order to achieve reduction in free energy. Similar particles larger than r_c will continue to grow [42].

Consider the rate of nucleation J so the number of nuclei formed per unit time per unit volume can be expressed in the form of Arrhenius reaction velocity [42]

$$J = D \exp(-\Delta G / K_B T_c)$$
(2-6)

- K_B : Boltzmann constant.
- D : Pre-exponential constant.
- T_c : Absolute temperature.

The basic Gibbs-Thomson relationship for a non-electrolyte may be written as:

Where S is defined by equation (2-8):

$$S = C/C^*$$
(2-8)

Where

C : Concentration of solution.

C* : Equilibrium saturation.

v: is the molecular volume

Hence, from equation (2-5):

And from equation (2-6):

$$J = D \exp\left[\frac{16\pi\gamma^{3}v^{2}}{3K_{B}^{3}T_{c}^{3}(\ln S)^{2}}\right] \qquad(2-11)$$

This equation indicates that three main variables govern the rate of nucleation [42]:

- Temperature (T_c) .
- Degree of supersaturation (S).
- Interfacial tension (γ) .

Equation (2-11) may be rearranged to give:

2-6 Supersaturation

The difference in chemical potential between two phases (phase of solution and phase of crystal) represents supersaturation and it is the main driving force of nucleation which it is given in the following equation [48]:

 $\Delta \mu$: The driving force.

 μ_m : Chemical potential of solution phase.

 μ_c : Chemical potential of crystal phase.

Following thermodynamics equation (2-13) can be expressed as:

Where (S) the supersaturation ratio.

When $\Delta \mu > 0$ the solution is said to be supersaturated, meaning that nucleation and/or growth is possible, whereas when $\Delta \mu < 0$ the solution will be undersaturated and dissolution will take place. The form of the supersaturation ratio will change depending on the system considered (i.e., gas/solid, solution/solid, melt/solid). For nucleation and growth from solutions it takes the following form [41]:

$$S = \frac{\Pi_{a_i}^{n_i}}{\Pi_{a_{i.e}}^{n_i}}$$
(2-15)

Where

 n_i : The number of *i*th ions in the molecule of the crystal.

 a_i , $a_{i,e}$: Actual and equilibrium activities of the *i* molecule in the crystal.

2-7 Habit of crystal

The modification of habit is a variation in the relative sizes of faces of a particular crystal [42]. The most prominent face of a crystal is the slowest growing, while the smallest face is the fastest growing [49]. Habitus is used to denote characteristic polyhedral form that a particular crystal species generally exhibit, such as isotropic or bulky, prismatic, tabular, bladed, lamellae, etc. This is principally due to anisotropy involved in bonding in the crystal structure [50].

The morphology of crystal is very important because it can determine many properties of a material, such as vapor pressure, shelf life, bioavailability, solubility, and density [51,33]. The morphology of a crystal depends on the growth rates of each of the crystal faces present. According to the Bravais rule, the important faces governing the crystal morphology are those with the highest reticular densities and the greatest interplanar distances (d_{hkl}) [42]. The imperfections become isolated into defective regions surrounded by large volumes of high perfection, when the crystal grows with a bulk habit.

In the crystals, which they grow as needles or plates, the growth dislocations propagate along the principal growth directions and the crystals remain imperfect [14].

Changes in crystals habit, which naturally grow as plates or needles can be achieved by any one of the following ways: changing the temperature on growth, changing the pH of the solution, adding a habit modifying agent, impurities and additives, changing the solvent and effect of light [52].

2-8 Crystal structure of CuSO₄.5H₂O

Copper sulfate pentahydrate belongs to the space group $C_i^{\ l}$ with two formula units per unit cell. Chalchanthite Group (Triclinic: PĪ) [21]. Two types of water molecules are found in the crystal. In this crystal copper atoms as presented in figure (2.7) are coordinated to a distorted octahedron of six oxygen atoms, four sort bond (2 Å) with an oxygen atom of $(H_2O)_1$ in a nearly square plane configuration and two Cu- $O(SO_4)^{2-}$ bonds perpendicular to the square plane [18,53]. The Cu- $O(H_2O)_1$, bonds being stronger than the Cu-O(SO_4) bonds, the complex molecule Cu(H₂O)₄ is nearly independent [21]. CuO₆ octahedra are distorted because the copper ion Cu²⁺ in the electronic configuration d^9 exhibits the Jahn–Teller effect: the average bond lengths between copper atoms and oxygen atoms of water molecules is 1.958 Å, while the bond length between copper atoms and oxygen atoms of sulfate (SO₄) is 2.385 Å [53,18]. In this structure the sulfate (SO₄)²⁻ ions act as bidentate ligands bridging two Cu(H₂O) ions [21].



Fig. (2.7): Scheme structure bonds in copper sulfate pentahydrate [21].

2-9 X-ray diffraction

X-ray diffraction (XRD) is an important technique in the field of materials characterization and it is a one of the most well-known methods for studying the structure of bulk materials.

X-rays are electromagnetic radiation which have a high-energy ranging from about 200 eV to 1 MeV, which puts them between gamma rays (γ -rays) and ultraviolet UV-rays in the electromagnetic spectrum. X-rays have wavelengths of about 0.01-10 nm [54].

The principle of Bragg's condition normally depends on the interference between reflected rays [55]:

where d is the spacing between atomic planes, θ is the angle of incidence from the sample surface and *n* is an integer giving the diffraction order, λ the wavelength of X-ray radiation.

Figure (2.8) shows a representation of incident rays interacting with the different crystal planes. Since the details of the diffraction pattern are due to the specific nature of the crystal, diffraction can be used to determine the crystal structure.



Fig. (2.8): Reflected X-rays in a Crystal [55].

The triclinic system has no axes of symmetry " $a\neq b\neq c$, $\alpha\neq\beta\neq\gamma$ ". The perpendicular distance between sequent planes of a hkl series is denoted as d_{hkl} . The formula for calculating interplanar spacings d_{hkl} for triclinic system is [55]:

2-10 Optical Properties

The study of the optical properties of a material is important because all materials may be related to their atomic structure, electronic band structure, electrical properties, and the use of materials in optical applications such as interference filters coating requires accurate knowledge of their optical constants over a wide range of wavelengths.

The study of the optical properties of a material is important because the optical properties of all materials may be related to their atomic structure, electronic band structure and electrical properties. Also, the use of materials in optical applications such as interference filters and reflective coating requires accurate knowledge of their optical constants over a wide range of wavelengths.

2-11 Transmittance (T)

Transmittance (T) is given by ratio of the intensity of the rays (I_T) transmitting through the crystal to the intensity of the incident rays (I_o) as follows [56]:

$T = I_T / I_o$	(2-18)
1 / -0	(

2-12 Fundamental absorption

The fundamental absorption causes a transition of an electron from the valence band to the conduction band. The fundamental absorption, which manifests itself by a rapid rise in absorption, can be used to determine the energy gap [57].

The cut off wavelength λ_c is the fundamental absorption edge, that occurs when incident photon energy equals the forbidden gap energy (E_g) and it is given by the relation [56]:

$$\lambda_{\rm c} \,({\rm nm}) = 1240/E_{\rm g} \,({\rm eV})$$
(2-19)

2-13 The electronic transitions and optical energy gap (Eg)

There are two types of electronic transitions which can be distinguished, direct and indirect, depending on the lower location point in conduction band, and upper point of valance band [58].

The direct transition occurs between top of valence band (E_v) and bottom of conduction band (E_c) (vertical transition) at same value of wave vector ($\Delta \vec{K} = 0$)

The allowed direct transition described by the following relation [58]

Where:

B: is the inversely proportional to amorphousity. α : is the absorption coefficient, measured by (cm⁻¹). hv: is the photon energy. E_g: is the energy gap.

The forbidden direct transition is described by the following relation [58]

$$\alpha h \upsilon = B (h \upsilon - E_g)^{3/2}$$
(2-21)

In the indirect transition there is a large momentum difference between the points to which the transition takes place in the valence and conduction bands [59].

The allowed indirect transition described by the following relation

While, the forbidden indirect transitions described by the following relation [59]

Experimentally, it is possible to differentiate between direct and indirect processes by the level of the absorption coefficient (α), (α) takes values from (>10⁴ cm⁻¹) for direct transitions and (<10⁴ cm⁻¹) for indirect transitions at the absorption edge [59].

The term "band gap" refers to the energy difference between the top of the valence band to the bottom of the conduction band. Electrons are able to jump from one band to another. In order for an electron to jump from a valence band to a conduction band, it requires a specific minimum amount of energy for the transition, the band gap energy. The band gap energy of insulators is high (> 4 eV), but lower for semiconductors (< 3 eV) [60].

2-14 Absorption coefficient (α)

Absorption coefficient can be defined as the decreasing ratio in incident ray energy in distance unit toward wave diffusion inside the medium [61].

The absorption coefficient (α) can be calculated as follows:

$$\alpha = 2.303 \left(\frac{A}{t}\right) \tag{2-24}$$

A: Absorbance.

t: Thickness.

2-15 Infrared (IR) spectroscopy

Infrared (IR) spectroscopy is used to study the vibrational motions of molecules and provides valuable information on structure and molecular conformation in the solid state [62,56]. It turns out that different motions among different groups of atoms cause the molecule to absorb different amounts of energy. Studying these transitions can sometimes allow us to determine what kinds of atoms are bonded or grouped in an unknown compound, which in turn gives clues to the molecular structure [62]. Like a fingerprint no two unique molecular structures produce the same infrared spectrum [63].

Absorption of energy in the infrared region ($\bar{\nu} = 4000-400 \text{ cm}^{-1}$) arises from changes in the vibrational energy of the molecules. There are two types of vibrations that cause absorptions in an IR spectrum. "Stretching" involves rhythmical displacement along the bond axis such that the interatomic distance alternately increases and decreases as in figure (2.9 a). "Bending" involves a change in bond angle between two bonds having a common atom as shown in figure (2.9 b).



Fig. (2.9): Stretching and bending vibrations [62].

One important condition is that only those vibrations that produce a change in the electric dipole moment of the molecule will be observed in the infrared spectrum [62].

Fourier-transform infrared (FTIR) spectroscopy is based on the idea of the interference of radiation between two beams to yield an interferogram. The latter is a signal produced as a function of the change of path length between the two beams. The two domains of distance and frequency are inter convertible by the mathematical method of Fouriertransformation.

The basic components of an FTIR spectrometer are shown schematically in figure (2.10). The radiation emerging from the source passes through an interferometer to the sample before reaching a detector. Upon amplification of the signal, in which high-frequency contributions have been eliminated by a filter, the data are converted to digital form by an analog-to-digital converter and transferred to the computer for Fouriertransformation [64].



Fig. (2.10): Basic components of an FTIR spectrometer [64].

In general, infrared spectroscopic techniques are strong, inexpensive, and require only small quantities of a compound and very little sample preparation [64]. FTIR can provide some information such as it identifying unknown materials, determining the quality or consistency of a sample and it can determine the amount of components in a mixture [62].

2-16 Polarizing microscope (PM)

A microscope is able to provide simultaneous physical, chemical, and crystallographic data on particles down to 500 nm and this would surely be hailed as an unbelievable tool. The polarized light microscope has demonstrated its value as an indispensable analytical instrument. Figure (2.11) shows interaction of polarized light with an anisotropic crystal [65].



Fig. (2.11): Interaction of polarized light with an anisotropic crystal [65].



3-1 Introduction

This chapter describes the growth procedure of copper sulfate pentahydrate (CSP) single crystals by slow evaporation technique. It also includes the specifications of the starting materials, the batch of the growth experiments and the description of the techniques that are followed to characterize the prepared crystal samples, such as X-Ray diffraction, Fourier Transform Infrared (FTIR), UV-Visible spectroscopy and polarizing microscope.

Figure (3.1) shows the schematic representation steps of the experimental procedure in present study.

3-2 Materials

3-2-1 Copper sulfate pentahydrate

Copper sulfate pentahydrate is a distinctive blue colour and it is the one first compound used by many chemists because it has many industrial applications [69].

The starting material for crystal growth is copper sulfate $CuSO_4.5H_2O$. Which is bright blue powder supplied by [BDH Chemicals Ltd Poole England] with "minimum assay (ex Cu) 98.5%, maximum limits of impurities, Alkalis (sulfated) 0.5%, Chloride (Cl) 0.005%, Iron (Fe) 0.08%,". Table (3.1) presents some of its properties.



Fig. (3.1): Schematic representation of the steps of the experimental procedure for crystal growth used in the present study.

Chemical formula	CuSO ₄ .5H ₂ O
Crystal Structure	Triclinic
Molecular Weight g/mol	249.68
Purity %	98.5
Solubility g/100 ml H ₂ O	22 at 25 °C
Covalent Radius Pm	132
Melting point °C	110

Table (3.1): Some properties of copper sulfate pentahydrate [67,68].

3-2-2 Type of solvent

i. Distilled water

Double distilled water is used to dissolve the copper sulfate in first batch.

ii. Sulfuric acid solution

Sulfuric acid solution is used as a solvent in the second batch with desired molarity. To prepare 1000 ml of 1 M H_2SO_4 solution from H_2SO_4 of 98% concentration and the specific gravity (SG) is 1.84 g/ml, the following calculations have been done :

$$M_{1} = \frac{\% \times SG \times 1000 \text{ ml}}{M.Wt} \qquad(3-1)$$
$$= \frac{98\% \times 1.84 \text{ g/ml} \times 1000 \text{ ml}}{98.08 \text{ g/M}} = 18.38 \text{ M}$$

Hence the volume of concentrated H_2SO_4 required to prepare the solution is calculation by using dilution law:

 $V_1. M_1 = V_2. M_2$ (3-2) $V_1 = \frac{V_2. M_2}{M_1}$

$$=\frac{1000 \text{ ml}\times 1M}{18.38 \text{ M}}=54.41 \text{ ml}$$

Where M_1 is the molarity of sulfuric acid, V_1 is a volume of sulfuric acid. The V_2 and M_2 are volume and molarity of diluted sulfuric acid respectively. So, the volume of H_2SO_4 (54.41 ml) is completed to 1000 ml of distilled water.

iii. Magnetic water

Magnetic water is prepared from distilled water by putting the water between the poles of magnet for (3 hours), then it is used as a solvent in the third batch. Figure (3.2) shows the magnet used in our study and the relation between magnetic field and the distance between the pole magnetic. The magnetic flux density is measured by Gauss/Tesla meter type NV621 made by NVIS-Technology shown in figure (3.3) and it is found to be 500 Gause in the center.



Fig. (3.2): (a): Homemade magnetic arrangement used in the current study to prepare magnetic water. (b): The relation between magnetic field and the distance between the magnetic poles.



Fig. (3.3): Gauss/Tesla Meter.

3-3 Crystal growth

The important stage in the solution growth is the preparation of the solution to grow the desired crystal. The crystals of the present work have been grown by the solution technique using slow evaporation method. Figure (3.4) shows a simple sketch of the solution growth process to grow single crystals. Two compound are mixed together. The first compound is the solute which must be grown as single crystal and the second compound is the solvent. The prepared solution is kept in the undisturbed place. After some time the formation of crystals can be observed. Then larger crystal was obtained by slow evaporation. Finally the excess solution is removed.

The desired weight of CuSO₄.5H₂O required to prepare the solution is given by:

$$W_t = \frac{M.V.M_{wt}}{1000}$$
(3-4)

Where M is the required molar concentration of the solution, M_{wt} : is the molecular weight of the material copper sulfate pentahydrate (g/mol), W_t is the weight (g) and V *is* the volume of solvent (ml).



Fig. (3.4): Schematic representation of the solution growth by slow evaporation technique [11].

3-4 Crystal growth from different solvent

Certain weights of copper sulfate pentahydrate CSP powder are dissolved in (100 ml) of (double distilled water, sulfuric acid of 1 M and magnetic water) at different temperatures to obtain the specific molarity. Table (3.2) shows the weights and molarity for different solvent. Each of the prepared solution was stirred well to yield a homogeneous mixture of solution by using magnetic stirrer. The solution of CuSO₄.5H₂O was filtered using filter paper to remove undissolved materials and dust particles. Then the copper sulfate pentahydrate solution was then poured into another clean beaker and covered with paper provided with some holes for growth. After the process of slow evaporation, the solute solubility is changed and the nucleation starts then the growth of the nucleus resulted a large copper sulfate crystals.

Types of solvent	Weights (g)	Molarity (M)
Distilled water	6.24	0.25
	12.48	0.5
	24.96	1
	37.45	1.5
	49.93	2
	62.42	2.5
H ₂ SO ₄ acid	5	0.2
	10	0.4
	15	0.6
	20	0.8
	25	1
Magnetic water	6.24	0.25
	12.48	0.5
	24.96	1
	37.45	1.5
	49.93	2

Table (3.2): Weights and molarity of copper sulfate pentahydrate.

3-5 Characterization techniques

3-5-1 Structural properties measurements:

(3-5-1-1) X-Ray diffraction

XRD diffraction is used to identify the structure of crystal. The X-ray diffracttometer used in this study was XRD 6000 made by Shimadzu (Japan), which has the following properties:

- 1. Source: Cu kα, Wavelength 1.5406 Å.
- 2. Voltage 40 KV.
- 3. Current 30 mA.
- 4. Axis Theta–2 Theta.

- 5. Scan range (10–80) deg.
- 6. Step 0.05 deg.
- 7. Speed 5.000 deg./min.

Figure (3.5) shows the photograph of XRD diffraction.



Fig. (3.5): Photograph of X-ray diffraction.



Fig. (3.6): Diagram of X-Ray equipment.

<u>3-5-1-2 Fourier Transform Infrared (FTIR)</u>

The FTIR spectra for the powdered samples in KBr medium were recorded in the range of wave number from 400 cm^{-1} to 4000 cm^{-1} using

IRAffinity-1 spectrophotometer made by Shimadzu, Japanese company. Figure (3.6) shows the Photograph of FTIR instrument used.



Fig. (3.7): Photograph of FTIR instrument used.

3-5-2 Optical properties measurements

<u>3-5-2-1 UV-Visible spectroscopy</u>

Ultraviolet-visible spectroscopy (UV/VIS) is also known as electronic spectroscopy [8]. The spectra of transmittance for the single crystal of copper sulfate pentahydrate (CSP) were recorded for the wavelengths (200-800) nm using UV–Visible 1800 Double beam spectrophotometer made by Shimadzu, Japanese company. Figure (3.7) shows the photograph of UV-Visible 1800 double beam spectrophotometer.

A Computer program origin 8.5 was used to obtain of the energy gap crystals.



Fig. (3.8): Photograph of UV- Visible 1800 double beam spectrophotometer.

The single crystals were polished by using a soft filter paper placed on glass plate. Few drops of distilled water were added on the filter paper before starting the polishing process which can be achieved throughout rubbing the sample gently by moving it continuously on the filter paper at 8-like shape trajectory until getting the required thickness of 2 mm.

3-5-2-2 Polarizing microscope (PM)

Hot-stage microscopy is an analytical mechanism which combines the best properties of microscopy and thermal analysis to enable the characterization of the physical properties of materials as a function of temperature. Hot-stage microscopy may be used for the solid-state characterization of bulk drugs, evaluation of crystal forms and hydrates, and other physio-chemical properties [69].

Some of the grown crystals of the current study were scanned using polarized optical microscope provided with heating stage to study the changes in the structure of these crystals when subjected to heat. The polarizing microscope used in this study was BL (model MPL-1), Italy company. This type of optical microscopes differs from ordinary microscope features by additional two equipment, namely the polarizer and analyzer: The polarizer should be placed below the condenser and the analyzer should be above the objective. The polarizer is rotatable 360° and the vibration direction of the polarizer should go side to side relatively to the observant and go vertically for an analyzer.

Chapter Four

Results, Discussion and Conclusions
4-1 Introduction

This chapter explains the results and discussions of the crystal growth and the structural properties (XRD analysis, calculation parameters of unit cell, and FTIR), and optical properties (UV-Vis and polarizing microscope).

4-2 Time of crystallization and size of grown (CSP) crystals

Single crystal of copper sulfate pentahydrate (CSP) were successfully grown at room temperature by the slow evaporation solution growth technique.

4-2-1 Time of crystallization and size of grown crystals using double distilled water as a solvent

Blue single crystals were obtained by spontaneous nucleation from the mother solution. The time of nucleation and the size of large crystal are shown in table (4.1).

Table (4.1): Molarity of solutions and time of crystallization of growncrystals and size of large crystals using distilled water.

Molarity (M)	Temperature of solution during its preparation (°C)	Time of starting of nucleation (days)	Time of completion of crystal (days)	Size of large crystal (mm ³)
0.25	R. T.	78	82	(39×12×3)
0.5	R. T.	76	91	(33.05×30.5×4.7)
1	R. T.	55	57	(21.6×19.38×3)
1.5	R. T.	2	42	(19.12×15.3×5.5)
1.5	59	10	39	(25.6×21.36×7)
2	27	2	47	Small seeds
2	50	1	50	Small seeds
2.5	40	The same day	38	Small seeds

The relation between the molarity of samples and the beginning of nucleation is shown in figure (4.1). The appearance and shape of crystals were grown from distilled water are shown in table (4.2). The photographs of grown single crystal from distilled water is shown in figure (4.2).



Fig. (4.1): The relation between the molarity of samples and beginning of nucleation (solvent is distilled water).

Molarity (M)	Temperature of solution during its preparation (°C)	Appearance and shape of crystals
0.25	R. T.	Had no distinction faces.
0.5	R. T.	Had distinction faces but not complete.
1	R. T.	Had shape complete faces (tetrahedron shape).
1.5	R. T.	Had many crystal and had different shape some of it is complete and other isn't.
1.5	59	Had appearance as twinned crystal resulting from imperfect crystal growth or deformed nuclei because agglomerated crystals continued to grow after agglomeration.
2	27 and 50	Had so many nuclei have small size.
2.5	40	Had so many nuclei have small size.

Table (4.2): Appearance and shape of crystals (solvent is distilled water).



Fig. (4.2): Photographs of grown single crystals using distilled water as a solvent.

Single crystals were grown by putting the best seed in the mother solution which had molarity of (1.5 M-R. T., 1.5 M-59 °C, 2 M-27 °C, 2 M-50 °C and 2.5 M-40 °C) after (9, 14, 9, 14 and 11) days respectively. The size of crystals were [($14.5 \times 14.06 \times 3.11$), ($11.58 \times 12.5 \times 5$), ($11.5 \times 15 \times 4$), ($15.56 \times 20.14 \times 6.78$), ($23.8 \times 20.3 \times 5.54$)] mm³ as shown in the figure (4.3).



Fig. (4.3): Photographs of grown single crystals by seeds.

Figure (4.3), it is noticed that the shape of crystals seeds is tetrahedron had distinctive and complete faces. The optimum condition for the growth of the best crystal was (1 M).

4-2-2 Time of crystallization and size of grown crystals using sulfuric acid as a solvent

Blue crystals were obtained by spontaneous nucleation from the mother solution. The time of nucleation and the size of large crystal are shown in table (4.3). The prepared solution was at room temperature.

Table (4.3): Molarity of solutions and time of crystallization of grown crystals and size of large crystals using H₂SO₄ acid.

Temperature of solution during its preparation (R. T.) Molarity (M)	Time of starting of nucleation (days)	Time of completion of crystal (days)	Size of large crystal (mm ³)
0.2	75	98	(34.7×20.3×6.54)
0.4	56	90	(50.68×23.4×8.3)
0.6	46	67	(17.4×37.6×6.7)
0.8	35	46	(24.14×15×7.7)
1	26	35	(14.5×34.11×42.3)

The relation between the molarity of samples and the beginning of nucleation is shown in figure (4.4). The appearance and shape of crystals were grown from H_2SO_4 acid shown in table (4.4). The photographs of grown single crystal is shown in figure (4.5). The optimum condition for the growth of best crystal was (0.8 M).



Fig. (4.4): The relation between the molarity of samples and beginning of nucleation (solvent is H_2SO_4 acid).

Molarity (M)	Appearance and shape of crystals
0.2	Had no complete faces and high frailty.
0.4	Had no distinction faces and had frailty.
0.6	Had distinction faces but not complete.
0.8	Had distinction and complete faces (tetrahedron shape).
1	Had many crystal, some of it had complete shape and
	others is not.

Table (4.4): Appearance and shape of crystals (solvent is H₂SO₄ acid).

The H_2SO_4 acid can be considered as a habit modifier for (CSP) crystals because it decreases the pH value in the solution and excesses of SO_4 anion. At low pH values, chemical impurities played the predominant role. Their entry into the growing crystal was increased with decreasing pH. From the review of figure (4.5) it is clearly shows that the growth rate of all faces decreased with reducing molarity of (CSP) solution this behavior is in agreement with the behavior of triglycine sulfate (TGS) crystal [4].



Fig. (4.5): Photographs of grown single crystal using sulfuric acid as a solvent.

4-2-3 Time of crystallization and size of grown crystals using magnetic water as a solvent

Blue single crystals were obtained by spontaneous nucleation from the mother solution. The time of nucleation and the size of large crystal are shown in table (4.5).

0.25

0.5

1

1.5

2

R. T.

R. T.

R. T.

R. T.

40

(20.9×18×2.7)

(18.1×16.3×3.6)

(42.4×27.36×7.5) (27.68×23.74×9.1)

(20×9×7.1)

crystals and size of large crystals using magnetic water.						
Molarity (M)	Temperature of solution during its preparation (°C)	Time of starting of nucleation (days)	Time of completion of crystal (days)	Size of large crystal (mm ³)		

41

38

25

19

1

43

44

37

35 34

Table (4.5): Molarity of solutions and time of crystallization of growncrystals and size of large crystals using magnetic water.

The relation between the molarity of samples and the beginning of nucleation is shown in figure (4.6). The appearance and shape of crystals were grown from magnetic water shown in table (4.6). The photographs of grown single crystal from magnetic water are shown in figure (4.7).



Fig. (4.6): The relation between the molarity of samples and beginning of nucleation (solvent is magnetic water).

Table (4.6): Appearance and shape of crystals (solvent is magnetic

water).

Molarity (M)	Temperature of solution during its preparation (°C)	Appearance and shape of crystals
0.25	R. T.	Had distinction faces.
0.5	R. T.	Had distinction faces but not complete.
1	R. T.	Had shape complete faces in one (tetrahedron shape), and other isn't distinction.
1.5	R. T.	Had many crystal as a agglomeration.
2	40	Had so many nuclei have small size and had different shape some of it is complete faces and other is not.

The magnetic water did not affect the improvement of the morphology of (CSP) crystals because the copper sulfate pentahydrate is a paramagnetic material, and its atoms possess permanent magnetic dipole moment (have strong magnetic field around a paramagnetic ions) [26,70]. The magnetic field leads to reduction in surface tension of water [71], thus it leads to a decrease in the interfacial tension, and the decrease in the interfacial tension is expected to produce an increase in the nucleation rate [33,54]. It was found that magnetic treatment for the water increased precipitation (CSP), this result is in agreement with precipitation behavior of calcium carbonate (CaCO₃) reported by Saksono et al. [72].

From figures (4.1), (4.4) and (4.6) can be seen a relationship between the grown time and the molarity in all cases. It was found that the time of beginning nucleation decreases by increasing the molarity. Noted that the rate of nucleation increases when the increase of molarity that belongs to the increases in supersaturation are produce an increase in nucleation rate [73].



Fig (4.7): Photographs of grown single crystals using magnetic water as a solvent.

The process of crystal growth from solution is a complex process that controlling several factors affect in the process of growth. These factors may be internal factors such as (the crystal structure, surface structures and crystal defects were formed during the process of growth), or may be external factors such as (supersaturation, the nature of the solvent, solution composition, impurities, physical conditions (temperature, pressure, magnetic fields, ultrasound, etc.) [4]. From the above findings, it can be noted that some crystals which are grown from (distilled water, H_2SO_4 acid and magnetic water) have complete faces while others have incomplete faces depending on the conditions of grown and medium of crystallization [42]. The size of crystal depends on the rate of nucleation and the growth, whereas the morphology of a crystal is a result of altering the relative growth rates of the crystal faces [33]. When the rate of nucleation is slow the growth results in a single nuclei. If the nucleation is started in a single nucleus it will grow faster than the nucleation of many nuclei [3].

4-3 XRD analysis

4-3-1 Single crystal XRD of crystals grown using distilled water as solvent

Figure (4.8) shows the XRD patterns of (CSP) single crystals grown by using distilled water at different molarity values (1.5- R. T., 1.5-59 °C, 2- 27 °C, and 2.5- 40 °C) M. It can be noticed in figure (4.8) that the patterns exhibit diffraction peaks around ($2\theta \sim 15^{\circ}$, 60° , 37° and 16°) referred to ($\overline{1}01$), (321), ($\overline{1}22$) and (020) directions respectively which is in agreement with the International Center for Diffraction Data (ICDD) card number 11-0646 shown in figure (4.27). The observed intense and sharp narrow peak in each XRD pattern is evidence of the formation of single crystals. The difference in the occurrence of peaks belong to the difference of shapes and colors of crystals [31] and belong to selected plane crystal.



Fig. (4.8): XRD patterns of single crystals grown using distilled water as solvent.

4-3-2 Powder XRD analysis

X-ray diffraction patterns of the grown (CSP) crystals using distilled water, H_2SO_4 acid and magnetic water as a solvent, shown that the crystals belong to the triclinic system with parameters of unit cell different from one sample to another because it change in the molarities and differ in the type of solvent. The diffraction pattern contains various reflections corresponding to various crystallographic planes [74]. The sharp peaks in the XRD pattern show the good quality crystalline nature of the grown crystals [38,74]. The parameters of unit cell are in agreement with the International Center for Diffraction Data (ICDD) card file number 11-0646.

1. Powder XRD of crystals grown using distilled water as a solvent

Figures from (4.9) to (4.16) show the powder XRD (PXRD) patterns of (CSP) crystals grown at different molarities values (0.25 M, 0.5 M, 1 M, 1.5 M, 1.5 M -59 $^{\circ}$ C, 2 M-29 $^{\circ}$ C, 2 M-59 $^{\circ}$ C and 2.5 M-40 $^{\circ}$ C). The unit cell parameters for all samples are shown in table (4.7) and (4.8) and it calculated by using wincell program. This confirms the identity of the substance.



Fig. (4.9): PXRD patterns of crystal grown at 0.25 M using distilled water as a solvent.



Fig. (4.10): PXRD patterns of crystal grown at 0.5 M using distilled water as a solvent.



Fig. (4.11): PXRD patterns of crystal grown at 1 M using distilled water as a solvent.



Fig. (4.12): PXRD patterns of crystal grown at 1.5 M using distilled water as a solvent.



Fig. (4.13): PXRD patterns crystal grown at 1.5 M-59 °C using distilled water as a solvent.



Fig. (4.14): PXRD patterns of crystal grown at 2 M-27 °C using distilled water as a solvent.



Fig. (4.15): PXRD patterns of crystal grown at 2 M-50 °C using distilled water as a solvent.



Fig. (4.16): PXRD patterns of crystal grown at 2.5 M- 40 °C using distilled water as a solvent.

The highest peak of the samples (0.25 M, 0.5 M, 1.5 M, 1.5 M-59 °C and 2 M- 27 °C) occurs at $2\theta \sim 18^{\circ}$ corresponding to ($0\overline{1}1$) direction and the samples (1 M, 2 M-50 °C and 2.5 M) occurs at $2\theta \sim 22^{\circ}$ which is referred to (011) plane. From figures (4.12), (4.13), (4.14), (4.15), and (4.16), it is noticed that the intensity increases by increasing the heat. The difference in the occurrence of the peak belongs to preferred orientation of the surface on the another surface [75] also due to plane of grain not spherically in the powder so the reflections intensity were not equal in all direction [76]. Table (4.9) shows the strongest three peaks of X-ray diffraction data of crystals from distilled water at different molarities.

Table (4.7): Unit cell parameters for all samples of crystals group	own using	5
distilled water as a solvent at room temperature.		

Lattian	Standard	This work					
parameters	11-0646	0.25 M- R. T.	0.5 M- R. T.	1 M- R. T.	1.5 M- R. T.		
a (Å)	7.155	7.156	7.174	7.168	7.250		
b (Å)	10.71	10.28	10.74	10.69	10.88		
c (Å)	5.955	5.908	5.962	5.941	6.092		
α (deg.)	97.63	96.50	97.48	97.51	98.07		
β (deg.)	125.3	124.8	125.3	125.5	125.5		
γ (deg.)	94.32	94.41	94.46	94.39	94.20		

 Table (4.8): Unit cell parameters for all samples of crystals grown by

 heat using distilled water as a solvent.

Lattian	Standard	This work					
Lattice		1.5 M-	2 M-	2 M-	2.5 M-		
parameters	11-0040	59 °C	27 °C	50 °C	40 °C		
a (Å)	7.155	7.095	7.152	7.140	7.230		
b (Å)	10.71	10.67	10.67	10.67	10.78		
c (Å)	5.955	5.920	5.951	5.967	6.014		
α (deg.)	97.63	97.71	97.68	97.97	97.47		
β (deg.)	125.3	125.1	125.3	125.8	125.3		
γ (deg.)	94.32	94.35	94.27	93.99	94.45		

	Molarity (M)	Temperature of solution during its preparation (°C)	2 0 (deg)	(hkl)
			18.551	(011)
	0.25	рт	22.112	(011)
	0.23	К. І.	26.835	(211)
			18.701	(011)
	0.5	R. T.	22.164	(011)
Distilled			31.104	(200)
water			22.188	(011)
	1	R. T.	18.769	(011)
			16.077	(110)
	1.5	R. T.	18.693	(011)
			32.428	(130)
			26.911	(211)
	1.5		18.693	(011)
		59	32.503	(130)
			23.926	(121)
			18.693	(011)
	2	27	26.911	(211)
			23.926	(121)
			22.254	(011)
	2	50	18.693	(011)
			23.926	(121)
			22.230	(011)
	2.5	40	18.699	(011)
			23.893	(121)

Table (4.9): X-ray diffraction data for strongest three peak of crystals

 grown at different molarities using distilled water as a solvent.

2. Powder XRD of crystals grown using sulfuric acid as a solvent

Figure from (4.17) to (4.21) show the PXRD patterns of crystals grown using (H_2SO_4) and different molarities (0.2 M, 0.4 M, 0.6 M, 0.8 M, and 1 M). The unit cell parameters for all samples are shown in the table (4.10).



Fig. (4.17): PXRD patterns of crystal grown at 0.2 M using H_2SO_4 acid as a solvent.



Fig. (4.18): PXRD patterns of crystal grown at 0.4 M using H_2SO_4 acid as a solvent.



Fig. (4.19): PXRD patterns of crystal grown at 0.6 M using H₂SO₄ acid as a solvent.



Fig. (4.20): PXRD patterns of crystal grown at 0.8 M using H_2SO_4 acid as a solvent.



Fig. (4.21): Powder XRD pattern of crystal grown at 1 M using H_2SO_4 acid as a solvent.

From the figures, (4.17), (4.18), (4.19), (4.20) and (4.21), it can be noticed that strongest peak occur at $(2\theta \sim 18^{\circ})$ which is referred to as $(0\overline{1}1)$ for the molarity (0.4 M and 0.8 M), and it can be seen occurs at $(2\theta \sim 22^{\circ}, 25^{\circ} \text{ and } 31^{\circ})$ referred to $(\overline{1}\overline{2}1)$, (120) and $(1\overline{2}1)$ for molarity (0.2 M, 0.6 M and 1 M) respectively. This difference in the occurrence this peak belongs to preferred orientation of the surface on the another surface [75] also it belongs to change in bond lengths. Table (4.10) shows the strongest three peaks of X-ray diffraction data of crystals grown by using H₂SO₄ acid at different molarities.

Table (4.10): X-ray diffraction data for strongest three peak of crystals grown at different molarities using H₂SO₄ acid as a solvent.

	Molarity (M)	20 (deg)	(hkl)
		22.254	(121)
	0.2	29.310	(221)
		24.002	(121)
		18.844	(011)
	0.4	24.002	(121)
		16.152	(110)
H ₂ SO ₄ acid	0.6	25.088	(120)
		23.926	(121)
		18.986	(011)
	0.8	18.769	(011)
		16.152	(110)
		29.084	(131)
		31.776	(121)
	1	18.911	(011)
		32.286	(212)

Lattice	Standard	This work					
parameters	11-0646	0.2 M	0.4 M	0.6 M	0.8 M	1 M	
a (Å)	7.155	7.134	7.157	7.118	7.156	7.202	
b (Å)	10.71	10.72	10.70	10.69	10.72	10.85	
c (Å)	5.955	5.919	5.977	5.927	5.959	5.956	
α (deg.)	97.63	97.25	97.71	97.69	97.59	97.20	
β (deg.)	125.3	125.2	125.3	125.2	125.3	125.3	
γ (deg.)	94.32	94.66	94.19	94.40	94.30	94.41	

Table (4.11): Unit cell parameters for all samples of crystals grown using H_2SO_4 acid as a solvent.

3. Powder XRD of crystals grown using magnetic water as a solvent

Figures from (4.22) to (4.26) show the PXRD patterns of crystals which were grown using magnetic water as a solvent and different molarities (0.25 M, 0.5 M, 1 M, 1.5 M and 2 M). The unit cell parameters for all samples are shown in the table (4.13).



Fig. (4.22): PXRD pattern of crystal grown at 0.25 M using magnetic water as a solvent.



Fig. (4.23): PXRD pattern of crystal grown at 0.5 M using magnetic water as a solvent.



Fig. (4.24): PXRD pattern of (CSP) crystal grown at 1 M using magnetic water as a solvent.



Fig. (4.25): PXRD pattern of (CSP) crystal grown at 1.5 M using magnetic water as a solvent.



Fig. (4.26): PXRD pattern of (CSP) crystal grown at 2 M using magnetic water as a solvent.

From figures (4.22), (4.23), (4.24), (4.25),and (4.26), it is found that the intensity increases by increasing the molarity except the molarity 2 M. From above figures, it can be noticed that the strongest peak occur at $(2\theta \sim 18^{\circ})$ referred to $(0\overline{1}1)$ plane for the molarity (0.5 M, 1 M and 2 M), it can be seen occurs at $(2\theta \sim 16^{\circ} \text{ and } 15^{\circ})$ referred ($\overline{1}10$) and (100) plane for molarity (0.25 M and 1.5 M) respectively. This difference in occurrence this peak belong to preferred orientation of the surface on the another surface [75] also it belongs to change in bond lengths. Table (4.12) shows the strongest three peaks of X-ray diffraction data of crystals grown by using magnetic water at different molarities. **Table (4.12):** X-ray diffraction data for strongest three peak of crystalsgrown at different molarities using magnetic water as a solvent.

	Molarity (M)	Temperature of solution during its preparation (°C)	2 0 (deg)	(hkl)
			16.152	(110)
	0.25	R. T.	18.693	(011)
Magnetic			22.254	(121)
water			18.783	(011)
	0.5	R. T.	16.077	(110)
			22.188	(011)
		ъ	18.844	(011)
	1	R. T.	16.294	(110)
			31.851	(121)
			15.567	(100)
	1.5	R. T.	18.844	(011)
			22.405	(121)
			18.844	(011)
	2	40	19.061	(110)
			31.701	(121)

 Table (4.13): Unit cell parameters for all sample of crystals grown using magnetic water as a solvent.

Lattice	Standard	This work					
parameters	11-0646	0.25 M	0.5 M	1 M	1.5 M	2 M	
a (Å)	7.155	7.164	7.041	7.239	7.189	7.173	
b (Å)	10.71	10.72	10.98	10.68	10.77	10.70	
c (Å)	5.955	5.965	5.840	5.995	5.999	5.958	
α (deg.)	97.63	97.60	96.83	97.59	97.60	97.68	
β (deg.)	125.3	125.3	123.4	126.2	125.5	125.4	
γ (deg.)	94.32	94.386	93.826	94.525	94.579	94.343	

Fig. (4.27): (ICDD) card number 11-0646.

The H_2SO_4 acid causes increases the intensity of peaks of XRD for crystals grown using H_2SO_4 acid as a solvent comparing with crystals grown using distilled water. This reveals that the H_2SO_4 acid has brought a change in the internal structure of the crystal of SO_4 anion which is due to change in bond lengths.

It is also possible the sulfuric acid contained hydrogen peroxide so that it will have the oxidizing power to dissolve copper metal Cu^{+2} , that is shown in table (4.14). The magnetic water causes increases in the intensity too.

Figure (4.28) shows the scheme of unit cell parameters for the grown crystal of 1 M for each solvent (distilled water, H_2SO_4 acid and magnetic water) painted by using powder cell program, in which using atomic position for each atom in (CSP) crystal from standard and calculate the bond lengths and angles that shown in table (4.14) and (4.15). The molecules of water did not appear because the powder cell program is unable to take into account the positions of water molecules.

In table (4.14) and (4.15), it is clear that the magnetic water causes a decrease in the bonds lengths of Cu_2 - O_2 and S_1 - O_2 and an increase the O_1 - S_1 and O_3 - S_1 . Also leads to decrease the angles of bonds. The H₂SO₄ acid causes an increases in the bonds lengths, and leads to increases the angles of bonds.



Fig. (4.28): Atoms position in the unit cell for crystals grown using:

(a) Distilled water. (b) Magnetic water. (c) H_2SO_4 acid.

Where: \bigcirc = Cu, \bigcirc = O, \bigcirc = S

Table (4.14): Bond lengths of crystals 1 M from distilled water, H_2SO_4 acid and magnetic water.

		Bond lengths (Å)					
Atom 1	Atom 2	Distilled water	Magnetic water	H ₂ SO ₄ acid			
Cu2	O2	2.2979	2.2900	-			
S 1	O2	1.3750	1.3738	1.3876			
S 1	O4	1.6709	1.6873	1.6746			
01	S 1	1.6903	1.6948	1.7075			
03	S 1	1.5221	1.5298	1.5378			

Atom			Angles of bonds (deg.)				
Atom 1	2	Atom 3	Distilled water	Magnetic water	H ₂ SO ₄ acid		
Cu2	O2	S 1	132.3575	132.1909	-		
O2	S 1	O4	86.8967	86.2686	87.0402		
01	S 1	03	103.6471	103.0189	104.2031		

Table (4.15):	Angles	of bonds	of crystals	1 M.
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4-4 The FTIR results of grown crystal

Figures from (4.29) to (4.43) show the FTIR transmittance spectra obtained for crystals grown used (distilled water, H₂SO₄ acid and magnetic water) as a solvent at different molarities. As it appears the bands of absorption at the range $(3200-3800 \text{ cm}^{-1})$ and $(1600-1700 \text{ cm}^{-1})$ which refer to the water molecules H₂O in the structure of compound inorganic, this regions are due to O-H stretching and bending vibration respectively [64,18,77]. The O-H stretching vibration of HSO_4^- extends from (2000-2400 cm⁻¹) [75]. Water of hydration is easily distinguished from hydroxyl groups by the presence of the H-O-H bending motion which produces a medium band (often multicomponent) in the region 1600-1650 cm⁻¹ [78]. Bending of (S-O-H) for group HSO_4^- appears in the rang (1400-1600 cm⁻¹) [79]. SO₄ non-degenerate mode appears at 982 cm⁻¹ ¹ [33]. The vibration mode of metal ion Cu^{2+} appears at 867 cm⁻¹ [35]. The ion SO_4^{-2} appears at rang (1130-1080 cm⁻¹) and (680-610 cm⁻¹) [67]. The spectra from (431-499 cm⁻¹) represented the sulfate SO_4^{-2} [5]. The peaks at lower band values can be explained with the vibrations between O and nonmetal atoms [77].

4-4-1 FTIR for crystals grown using distilled water as a solvent

Figures from (4.29) to (4.34) show the FTIR transmittance spectra obtained for crystals grown using distilled water at different values of molarity (0.25 M, 0.5 M, 1 M, 1.5 M, 2 M and 2.5 M) respectively. Table (4.16) shows the comparison and functional group assignment of IR bands of CSP grown using distilled water as a solvent.



Fig. (4.29): FTIR transmittance spectrum of crystal grown using distilled water as a solvent at 0.25 M.



Fig. (4.30): FTIR transmittance spectrum of crystal grown using distilled water as a solvent at 0.5 M.



Fig. (4.31): FTIR transmittance spectrum of crystal grown using distilled water as a solvent at 1 M.



Fig. (4.32): FTIR transmittance spectrum of crystal grown using distilled water as a solvent at 1.5 M.



Fig. (4.33): FTIR transmittance spectrum of crystal grown using distilled water as a solvent at 2 M-27 °C.



Fig. (4.34): FTIR transmittance spectrum of crystal grown using distilled water as a solvent at 2.5 M-40 °C.

Table (4.16): IR bands of CSP crystals grown using distilled water as	a
solvent at different molarities.	

Wave number (cm ⁻¹)						Assignment
0.25 M	0.5 M	1 M	1.5 M	2 M	2.5 M	
		3103.46	3007.02			O-H stretching
		3128.54	3034.03			
		3169.04	3066.82			
		3199.91	3109.25			
3288.63	3288.63		3126.61			
	3385.07		3145.90	3383.14	3385.07	
3415.93	3415.93		3170.97	3421.72	3415.93	
3446.79	3448.72		3224.98	3441.01	3448.72	
3485.73			3240.41	3483.44		
			3304.06	3506.59		
			3321.42	3527.80		
			3344.57			
1629.85	1625.99	1629.85	1633.71	1631.78	1641.42	Bending vibration of
						O-H
						(H2O)
	1456.26					Bending of S-O-H
	1517.98	-	-			$(SO_4)^{-2}$
1537.27	1527.62				-	
	1541.12			1558.48		
1095.57	1099.43	1091.71	1143.79	1093.64	1105.21	Stretching vibration of S-O group
1147.65	1151.50	1151.50	1153.43	1157.29	1153.43	
115150			1166.86		1197.79	
1161.51			1195.87			
1201.65	1201.65	1201.65	1209.37	1203.58		
960.55	960.55	997.20	960.55	960.55		SO ₄ . non-degenerate mode
997.20	995.27		997.20	995.27	995.27	
785.03	785.03	887.26	786.96	729.09	873.75	Vibration mode of metal ion Cu ⁺²
						Cu-O-H
628.79	659.66	603.72	657.73	659.66	615.29	SO ₄ degenerate mode
659.66		634.58			657.73	
		659.66				
453.27	451.34	482.20	516	518	-	SO ₄ bending group of sulfate
487.99	487.99					

The difference in appearance of modes of ions (SO_4^{-2}) attributed to the chemical reactivity of copper salts on KBr windows [21].

4-4-2 FTIR for crystals grown using H₂SO₄ acid as a solvent

Figures from (4.35) to (4.39) show the FTIR transmittance spectra obtained for crystals grown using H_2SO_4 acid at different values of molarity (0.2 M, 0.4 M, 0.6 M, 0.8 M and 1 M) respectively.



Fig. (4.35): FTIR transmittance spectrum of crystal grown using H_2SO_4 as a solvent at 0.2 M.



Fig. (4.36): FTIR transmittance spectrum of crystal grown using H_2SO_4 as a solvent at 0.4 M.



Fig. (4.37): FTIR transmittance spectrum of crystal grown using H_2SO_4 as a solvent at 0.6 M.



Fig. (4.38): FTIR transmittance spectrum of crystal grown using H_2SO_4 as a solvent at 0.8 M.



Fig. (4.39): FTIR transmittance spectrum of crystal grown using H_2SO_4 as a solvent at 1 M.

Table (4.17) shows the comparison and the functional group assignments of IR bands for crystals grown using H_2SO_4 acid as a solvent. It is noticed that the metal ion Cu^{+2} Cu-O-H appears just in the molarity (0.2 M and 0.8 M) that belong to effect of H_2SO_4 acid.

Table (4.17): IR bands of CSP grown using H ₂ S	SO ₄ acid as a solvent at
different molarities.	

	Wave	e number (Assignment		
0.2 M	0.4 M	0.6 M	0.8 M	1 M	
3429.43	3088.03 325970	3332.99 3367.71 3402.43	3371.57 3385.07 3410.15	3309.85 3327.21	O-H stretching
2357.01	-	2362.80	2098.55 2357.01	-	Stretching O-H within HSO ₄
1633.71	1629.85	1577.77	1627.92 1577.77	1577.77	Bending of H-O-H
1525.69	1539.20	1539.20	1539.20	1539.20	Bending of S-O-H
1165.00 1192.01	1085.92 1141.86 1174.65 1205.51	1093.64 1155.36 1203.58	1097.50 1139.93 1157.29 1195.87	1155.36 1201.65	Stretching vibration of S-O group
999.13	962.48 987.55	995.27	993.34	987.55 993.34	SO ₄ . non-degenerate mode
873.75	-	-	777.31	-	Vibration mode of metal ion Cu ⁺² Cu-O-H
663.51	659.66	661.58	657.73	661.58	SO ₄ degenerate mode
451.34	447.49	449.41	-	-	SO_4^{-2} bending group of sulfate

4-4-3 FTIR for crystals grown using magnetic water as a solvent

Figures from (4.40) to (4.44) show the FTIR transmittance spectra obtained for crystals grown using magnetic water at different values of molarity (0.25, 0.5, 1, 1.5 and 2 M) respectively. Table (4.18) shows the comparison and the functional group assignments of IR bands for crystals.



Fig. (4.40): FTIR transmittance spectrum of crystal grown using magnetic water as a solvent at 0.25 M.



Fig. (4.41): FTIR transmittance spectrum of crystal grown using magnetic water as a solvent at 0.5 M.



Fig. (4.42): FTIR transmittance spectrum of crystal grown using magnetic water as a solvent at 1 M.



Fig. (4.43): FTIR transmittance spectrum of crystal grown using magnetic water as a solvent at 1.5 M



Fig. (4.44): FTIR transmittance spectrum of crystal grown using magnetic water as a solvent at 2 M.

From tables (4.16), (4.17) and (4.18), it is clearly seen that all the transmittance bonds of the above bonds shift to the higher or lower wavenumber with increasing molarity and with difference solvent this difference in occurrence this shift belong to the external factors such that (impurities, temperature, pressure) during growth of crystals.

Wave number (cm ⁻¹)					Assignment
0.25 M	0.5 M	1 M	1.5 M	2 M	
3059.10	3007.02		3093.82		O-H stretching
	3014.74				C
	3072.60				
3109.25	3122.75	3136.25	3107.32		
3145.90	3178.69	3145.90	3126.61		
		3157.47	3143.97		
		3172.90	3155.54		
		3199.91			
3209.55	3228.84	3207.62			
	3271.27			3311.78	
3450.65					
1629.85	1624.06	1672.28	1668.43	1635.64	Bending vibration of
2088.91	1676.14	2362.80	2083.12	1670.35	О-Н
2355.08			2360.87	2360.87	
1417.68					Bending of
1456.26					S-O-H
1512.19					
1529.55	1527.62	1539.20	1541.12	1541.12	
1591.27		1577.77	1575.84		
1083.99	1062.78		1091.71	1091.71	Stretching vibration of S-O group
1126.43	1111.00	1111.00	1101.35		
999.13	-	-	-	-	SO ₄ . non-degenerate mode
875.68	875.68	879.54	875.68	881.47	Vibration mode of metal ion Cu ⁺⁺ Cu-O-H
621.08	621.08 696.30	621.08	617.22	619.15	SO ₄ degenerate mod
-	424.34	443.63	449.41	468.70	SO_4^{-2} bending group of sulfate

 Table(4.18): IR bands of CSP grown using magnetic water as a solvent at different molarities.

From above, it was found that the intensity FTIR transmittance for crystals grown using H_2SO_4 acid as a solvent was lower than intensity FTIR transmittance for crystals grown using distilled water as a solvent, and the intensity FTIR transmittance for the crystals grown using magnetic water was lower than crystal from distilled water and higher from the H_2SO_4 acid. It is observed that the bond of metal ion Cu⁺² appears in the crystals grown using distilled water as a solvent and does not appear in the crystals grown using H_2SO_4 acid as a solvent and the appearance with less intensity in the crystal grown by using magnetic
water as a solvent that due to effect of solvents on change the bond length.

4-5 The UV-visible spectrum analysis of grown crystals

The UV-Visible measurement results involve computing transmission, absorption coefficient and energy gap for single crystals of (CSP) with different molarities and different solvent included (distilled water, sulfuric acid and magnetic water). The samples were prepared for measurement by cutting and polishing them into plates of a thickness (2 mm). The optical properties depend on the morphology or shape of crystals [32].

4-5-1 Optical Transmission Spectrum Analysis

Figure (4.45), (4.46) and (4.47) show the relation between transmittance and wavelength in the range of (200-800) nm for single crystal of (CSP) grown using (distilled water, H₂SO₄ acid and magnetic water) as a solvent. The transmittance for all samples of copper sulfate pentahydrate increases as the wavelength increases in the range of (275-470) nm, (277-487) nm and (275-470) nm respectively, then it decreases as the wavelength increases further. The cut-off of wavelength is shown in the table (4.19). There is an abnormal absorption spike at ~340 nm that may belong to distorted CuO₆ octahedral because the copper ion Cu⁺² in the electronic configuration d⁹ exhibits the Jahn-Teller effect [53,18]. The spectra show high transmittance in the ultraviolet and visible region but there is no transmittance in the infrared region. This is in agreement with the results reported by Anne et al. [35] and reported by Manomenova et al. [18].

The transmittance in the crystal grown using (distilled water and magnetic water) increases with the increase in the molarity of the solution and the molarity 1.5 M and 2 M has a maximum transmittance of nearly equal to 22%, 21.7% at the wavelength (475 nm and 337 nm) respectively. The transmittance in the crystal grown using H_2SO_4 acid increases with the decrease of the molarity and the molarity 0.8 has a maximum transmittance of nearly equal to 1.43% at the wavelength (472 nm).

The (CSP) crystals grown using distilled water as a solvent is transparent in the wavelength ranged between 300 nm and 530 nm and it can be used as optical bandpass filters in this range. This result is in agreement with the results reported by Anne et al. [35] and reported by Manomenova et al. [18]. The crystals grown using H_2SO_4 acid and magnetic water as a solvent is very transparent in the wavelength ranged (311-497) nm and (307-523) nm respectively.



Fig. (4.45): Transmittance (T%) versus wavelength (λ) of CSP single crystals grown using distilled water at different molarities.



Fig. (4.46): Transmittance (T%) versus wavelength (λ) of CSP single crystals grown using H₂SO₄ acid at different molarities.



Fig. (4.47): Transmittance (T%) versus wavelength (λ) of CSP single crystals grown using magnetic water at different molarities.

From figures (4.45),(4.46) and (4.47), it is noted that the H_2SO_4 acid causes a decrease in the transmittance, and the magnetic water causes a decreases in the transmittance but by lower rate.

4-5-2 Absorption coefficient (α)

The absorption coefficient was calculated using equation (2-24). Figures (4.48), (4.49) and (4.50) show the optical absorption coefficient (α) as a function of incident photon energy on (CSP) crystals grown using (distilled water, H₂SO₄ acid and magnetic water) as a solvent. It can be seen that CSP crystals has a value of absorption coefficient ($\alpha < 10^4$ cm⁻¹) which indicates the probability of the occurrence indirect transitions. At high and low energies, absorption coefficient is high. This means that there is a high possibility for electron transition. Consequently, the energy of the incident photon is enough to move the electron from the valence band to the conduction band, i.e. the energy of the incident photon is greater than the energy gap. Also, it has seen that absorption coefficient is the smallest at medium energies in the range (2.5-4.3) eV. This means that the possibility of electron transition is low because the energy of the incident photon is not sufficient to move the electron from the valence band to the conduction band (hu < E g) [80].

Also, it can be noticed that the absorption coefficient increases with decreasing the molarity in the crystals grow using distilled water and magnetic water, but in the crystals grow using H_2SO_4 acid increases with increasing molarity. It is clear that the H_2SO_4 acid and magnetic water cause increasing in the absorption coefficient.



Fig. (4.48): The relation between absorption coefficient and photon energy of single crystals grown using distilled water as a solvent.



Fig. (4.49): The relation between absorption coefficient and photon energy of single crystals grown using H_2SO_4 acid as a solvent.



Fig. (4.50): The relation between absorption coefficient and photon energy of single crystals grown using magnetic water as a solvent.

4-5-2 Optical energy gap

The energy gap values depend in general on the crystal structure, the arrangement and distribution of atoms in the crystal lattice, also affected by crystal regularity. The optical energy gap (E_g) was derived assuming the allowed indirect transitions between the edge of the valence and conduction band.

By plotting a graph between $(\alpha hv)^{1/2}$ and (hv) in eV, a straight line is obtained which gives the value of the indirect band gap. The extrapolation of the straight line to $(\alpha hv)^{1/2} = 0$ gives value of the indirect band gap of the material.

The energy gap for single crystals grown using distilled water as a solvent could be seen in figure (4.51). One can notice that the band gap value increases when the molarity increases. This increase in the band gap can be related to the structural modification of the single crystal with higher molarity. The allowed indirect band gap values in the range of (4.17-4.25) eV for the prepared samples, as shown in table (4.19), This result is in agreement with the results reported by Anne et al. [35]. The energy gap for single crystal grown using H_2SO_4 as a solvent could be seen in figure (4.52). The allowed indirect band gap value for molarity 0.8 M is 4.14 eV and the for 1 M is 4 eV. It found the energy gap decreasing by increase molarity. The energy gap for single crystal grown using magnetic water could be seen in figures (4.53). The allowed indirect band gap values range between 4.06 eV and 4.25 eV. It found the energy gap increase by increasing molarity. The equation (2-19) used to calculation the energy gap of all samples based on the values of cut-off wavelength, it is shown in table (4.19) the values energy gap.

Figures (4.51), (4.52) and (4.53), it can be seen that the acid (H_2SO_4) decreases energy gap, and the magnetic water decreases energy gap too but by lower rate.



Fig. (4.51): The relation between $(\alpha h \upsilon)^{1/2}$ and $(h \upsilon)$ of single crystal grown using distilled water as a solvent.



Fig. (4.52): The relation between $(\alpha h \upsilon)^{1/2}$ and $(h \upsilon)$ of single crystal grown using H_2SO_4 acid as a solvent.



Fig. (4.53): The relation between $(\alpha h \upsilon)^{1/2}$ and $(h \upsilon)$ of single crystal grown using magnetic water as a solvent.

Table (4.19): Cut-off of wavelength and energy gap by tauc and cut-off of single crystals grown using (distilled water, H₂SO₄ acid and magnetic water) as a solvent.

Solvent	Molarity (M)	E _g (eV) by tauc	Cut-off wavelength(nm)	E _g (eV) by cut-off
Distilled water	0.25 M	4.17	287	4.32
	0.5 M	4.19	283	4.38
	1 M	4.23	280	4.42
	1.5 M	4.25	279	4.44
	0.8 M	4.14	289	4.29
H ₂ SO ₄ acid	1 M	4	292	4.24
Magnetic water	0.25 M	4.06	289	4.29
	1 M	4.09	287	4.32
	1.5 M	4.22	283	4.38
	2 M	4.25	281	4.41

4-6 Polarizing microscope (PM) result analysis

Figures (4.54) to (4.62) show (CSP) crystal with molarity (1 M) grown by using distilled water at different temperature. The rate of temperature increase was 2 °C/min. and the magnification of the microscope was set to be 200X for all samples.

The temperatures shown in the figures have been chosen depending on the significant color change that occurs in the images of the sample due to water molecules loss.

Figures (4.54) and (4.55) show (CSP) crystal at the temperature (25 and 50 °C) respectively, it cannot be observed change in general features of crystal. Figure (4.56), (4.57), (4.58) and (4.59) represent (CSP) crystal at temperature (70 °C, 72 °C 74 °C and 76 °C) respectively, it can be seen that change in some sites of grain, and in the temperature (72 °C), it is clear that the (CSP) crystal loss some water molecules. Figure (4.60) shows the crystal at temperature (82 °C), it is clear that the crystal loses more of water molecules, and at temperature (92 °C) as shown in figure (4.61) it is not noticed any change in the color of crystal about the temperature (82 °C). At the temperature (150 °C) as shown in the figure (4.62), it was found more change in color crystals and loses all water molecules.



Fig. (4.54): CSP crystal at (25 °C).



Fig. (4.55): CSP crystal at (50 °C).



Fig. (4.56): CSP crystal at (70 °C).



Fig. (4.57): CSP crystal at (72 °C).



Fig. (4.58): CSP crystal at (74 °C).



Fig. (4.59): CSP crystal at (76 °C).



Fig. (4.60): CSP crystal at (82 °C).



Fig. (4.61): CSP crystal at (92 °C).



Fig. (4.62): CSP crystal at (150 °C).

4-7 Conclusions

1. The technique of slow evaporation for solution of $CuSO_4.5H_2O$ is suitable for grown crystals at room temperature.

2. The optimum condition for the growth of the best CSP crystal was 1 M for crystal grown using distilled water.

3. The nucleation time for all cases of grown CSP crystal decreases as the solution molarity increases.

4. The H_2SO_4 acid decreases the growing of various faceted samples.

5. The magnetic water did not improve the morphology of CSP crystal.

6. The XRD analysis confirms that the crystalline system for crystals (CSP) is triclinic, the parameters of the unit cell are in agreement with the values of (ICDD) card file number 11-0646.

7. From the FTIR, it was found that the H_2SO_4 acid and magnetic water lead to a decrease in the intensity of transmittance compared with the distilled water. It is observed that the increase of molarity indicates an increase in the intensity or shifting in the some sites of peaks.

8. From UV spectra, it is found the H_2SO_4 acid and magnetic water decrease the transmittance and energy gap. Also, it was found that the increase in molarity leads to increase in the transmittance and energy gap of crystals grown using distilled water and magnetic water, and they decrease by increasing the molarity at the crystal grown using H_2SO_4 acid.

9. The Polarizing microscope analysis shows that the CSP crystal lost all water molecules at the temperature (150 $^{\circ}$ C).

10. The crystals can be used as optical bandpass filters.

4.8 Future works

- Studying the electrical properties for copper sulfate pentahydrate crystals.
- Studying the properties of copper sulfate pentahydrate crystal by added type of impurities such as FeSO₄.
- Studying properties of crystals grown using water magnetic treatment for five hour.
- Studying the effect of (NH₄)₂SO₄ on grown (CSP) crystal.





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Published and Accepted Research Articles

1- Nabeel A. Bakr, Tariq A. Al-Dhahir and Saja B. Mohammed, "Growth of Copper Sulfate Pentahydrate Single crystals by Slow Evaporation Techniqe", Journal of Advances in Physics, Vol. 13, No. 2, Issn 2347-2487, pp. 4651-4656, March 2017.

2- Tariq A. Al-Dhahir, Nabeel A. Bakr and Saja B. Mohammed, "Influence of solvents on the growth of copper sulfate pentahydrate single crystals", Journal of Diyala for Pure science, Accepted for Publication, 2017.



تم انماء بلورات منفردة من كبريتات النحاس المائية (CSP) في ثلاث مجموعات مختلفة بتقنية التبخير البطىء في درجة حرارة الغرفة. تضمنت المجموعة الاولى انماء البلورات باستخدام الماء المقطر مرتين كمذيب بمولارية (M 0.25 M 0.5 M ، 1 M ، 0.5 M ، 1.5 M ، 1.5 M ، 1.5 M · (39× 12 ×3)] وبأبعاد (2.5 M-40 °C and 2 M- 50 °C ·2 M- 27 °C ·59 °C (25.6×21.36 (19.12×15.3×5.5) (21.6×19.38×3) (33.05×30.5×4.7) mm³ [$(23.8 \times 20.3 \times 5.54)$ ·($15.56 \times 20.14 \times 6.78$) ·($10 \times 17.2 \times 6.78$) ·×7) على التواليي. أما المجموعة الثانية فتضمنت دراسة تأثير حامض H₂SO₄ على انماء البـــلورات بمولاريــة (M and 0.8 M 0.6 M 0.4 M 0.2 M) وبأبعاد [(24.14×15×7.7) (17.4×37.6×6.7) (50.68×23.4×8.3) (34.7×20.3×6.54) (14.5×34.11×42.3)] mm³ على التوالي. أذ وجد ان نسبة انماء كل الوجوه البلورية تتناقص مع تناقص مولارية محلول (CSP). أما المجموعة الثالثة فتضمنت دراسة تأثير الماء الممغنط على انماء البلورات بمولارية (M ، 0.25 M ، 0.5 M ، 1.5 M ، 1.5 M ، 1.5 M ، 1.5 M M وبأبعاد [(X × 27.36 × 7.5) (18.1 × 16.3 × 3.6) (20.9 × 18 × 2.7) وبأبعاد (M mm³ [(20×9×7.1)،(27.68×23.74 ×9.1)] هلى التوالي. وجد ان الماء الممغنط لم يحسن المورفولوجيا لبلورات (CSP). تم تحليل البنية البلورية للبلورات التي نمت بثلاث دفعات بتقنية حيود الأشعة السينية. يبين فحص XRD ان نظام البلورات ثلاثي الميل (triclinic) وان قيم معلمات الشبيكة البلورية تتفق مع بطاقة (ICDD). تمت در اسة الانماط الاهتز ازية للبلورات المنماة أجريت بمطياف FTIR. وجد ان الحامض H₂SO₄ والماء الممغنط أدى الى زيادة شدة الامتصاصية مقارنة بالماء المقطر، وقد لوحظ ان ايون Cu⁺² Cu-O-H ظهر عند البلورات المنماة باستخدام الماء المقطر كمذيب وانعدام ظهوره في البلورات المنماة باستخدام حامض كمذيب مع ظهوره بشدة اقل في البلورات المنماة باستخدام الماء الممغنط كمذيب. در M $_2SO_4$ طيف UV-Visible لحساب معامل الامتصاص وفجوة الطاقة، وجد ان الحامض قد ادى الى نقصان قيم النفاذية، ولوحظ ان الماء الممغنط ادى الى نقصان في قيم النفاذية لكن بقيم اقل كذلك، أظهرت النتائج ان زيادة المولارية تؤدي الى زيادة النفاذية للبلورات المنماة باستخدام الماء المقطر والماء الممغنط كمذيبات. كذلك، وجد ان نقصان المولارية يؤدى الى زيادة النفاذية للبلورات المنماة باستخدام حامض H_2SO_4 كمذيب. معامل الامتصاص للبلورات المنماة باستخدام المذيبين الماء المقطر والماء الممغنط يقل بزيادة المولارية، بينما يزداد بزيادة المولارية في البلورات المنماة باستخدام المذيب حامض H_2SO_4 ، كما وجد ان الحامض يؤدي الى زيادة قيم معامل الامتصاص بالمقارنة مع الماء المقطر والماء الممغنط. كما لوحظ ان فجوة الطاقة تزداد بزيادة المولارية للبلورات المنماة باستخدام المذيبين الماء المقطر والماء الممغنط، لكنها تقل بزيادة المولارية للبلورات المنماة باستخدام المذيبين الحامض والماء المعنط، في البلورات المنماة باستخدام المذيب حامض H_2SO_4 عن البلورات المنماة باستخدام المذيبين الماء مناه باستخدام المذيبين الماء معامل والماء المعنط، في البلورات المنماة باستخدام المذيب الحامض H_2SO_4 . فجوة الطاقة تقل الماء المنماة باستخدام المذيب حامض H_2SO_4 عن البلورات المنماة باستخدام المذيبين في البلورات المنماة باستخدام المذيب حامض H_2SO_4 عن البلورات المنماة باستخدام المذيبين بزئيات الماء الممغنط. أوضح تحليل المجهر المستقطب ان بلورة (CSP) تفقد كل جزئيات الماء عند درجة حـرارة (C°).