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

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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 dimensions were $[(39 \times 12 \times 3), (33.05 \times 30.5 \times 4.7), (21.6 \times 19.38 \times 3),$ (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 H₂SO₄ 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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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)
μ _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)
Wt	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 pharmaceuticals. computers, infrared as detectors, frequency 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 solvent above the solution is higher 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

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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 revealed **UV-Vis** that spectra. spectra 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 $CuSO_{4.}5H_{2}O$ 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 NiSO₄.6H₂O and CuSO₄.5H₂O 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 H₂SO₄ 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.