Influence of Solvents on the Growth of Copper Sulfate Pentahydrate Single Crystals

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Abstract

Single crystals of copper sulfate pentahydrate (CSP) were grown up to (21.6×19.38×3 mm^3), (14.5×34.11×42.3 mm^3) and (42.4×27.36×7.5 mm^3) from aqueous solution by slow evaporation technique at room temperature using double distilled water, H_2SO_4 acid and magnetic water as solvents respectively. Structure analysis of grown crystals was carried out by X-ray diffraction technique. The study of the vibrational modes for the grown crystals was conducted by FTIR spectroscopy. It is observed that the H_2SO_4 acid led to the disappearance of Cu^{+2} metal ion (Cu-O-H) mode in crystal, while the magnetic water led to appearance of it with less intensity compared by appearing in the crystals grown using distilled water. The UV-Visible result shows that the crystals have cut-off at 280 nm, 292 nm and 287 nm, with optical energy gap (4.23 eV, 4 eV and 4.09 eV) for crystals grown using distilled water, diluted acid and magnetic water as a solvent respectively.

Keywords: Crystal Growth, Copper Sulfate Pentahydrate, Magnetic Water, Sulfuric acid, XRD, FTIR Spectroscopy, UV-Visible Spectroscopy.

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تأثير المذيبات على نماء بلورات منفردة من كبريتات النحاس المائية

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الخلاصة

تم انماء بلورات منفردة من كبريتات النحاس المائية (CSP) من محلولها المائي بتقنية التبخر البطئ عند درجة حرارة الغرفة باستخدام مذيب (ماء مقطر، حامض الكبريتيك H_2SO_4 وماء ممغنط) وبأبعاد [(3×19.38×21.6)، (14.5×34.11×42.3)، (42.4×27.36×7.5)] mm^3 على التوالي. تم تحليل البنية البلورية للبلورات بتقنية حيود الأشعة السينية. وتمت دراسة الانماط الاهتزازية للبلورات المنماة بمطياف FTIR. وجد ان الحامض H_2SO_4 والماء الممغنط أدى الى زيادة شدة الامتصاصية مقارنة بالماء المقطر، وقد لوحظ ان ايون Cu-O-H Cu^{+2} ظهر عند البلورات المنماة باستخدام الماء المقطر كمذيب وانعدام ظهوره في البلورات المنماة باستخدام حامض H_2SO_4 كمذيب مع ظهوره بشدة اقل في البلورات المنماة باستخدام الماء الممغنط كمذيب. درس طيف UV-Visible لحساب معـــامل الامتصاص وفجوة الطاقة. أوضحــت نتـــائج UV-Visible أن البلورات تمتلك قطع بالطول الموجي عند (280 nm, 292 nm and 287 nm)، كما ان فجوة الطاقة البصرية لبلورات (CSP) تساوي (4.23 eV, 4 eV and 4.09 eV) للبلورات المنماة باستخدام المذيب ماء مقطر، حامض الكبريتيك والماء الممغنط على التوالي.

الكلمات المفتاحية: أنماء بلوري، كبريتات النحاس المائية، ماء ممغنط، حامض الكبريتيك، حيود الاشعة السينية، مطيافية تحويل فورير للاشعة تحت الحمراء، مطيافية الاشعة فوق البنفسجية – المرئية.

Introduction

The crystals are unrecognized pillars of the modern technology. But its plays an important role in the electronic and photonic industry and fiber optic communications, which depend on materials/crystals such as polarizers, semiconductors, superconductors, radiation detectors, transducers, ferrites, ultrasonic amplifiers, 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 [1-3]. Copper sulfate pentahydrate (CSP) is an inorganic salt having a bright blue color. It crystallizes in triclinic system, and possesses centro-symmetry belonging to $C_{i.}^{1}$ space group [4,5]. In the last (45) years many results about the effect of magnetic field on the precipitation and crystallization of inorganic compounds have been presented in the scientific literature, but most of the experiments reported so far are rather qualitative and the results are sometimes contradictory. In 1999, Freitas et al. published a study of the influence of magnetic field on the crystallization of copper sulfate [6]. In the present investigation copper sulfate pentahydrate crystals were grown by slow evaporation technique from distilled water, diluted H_2SO_4 acid and magnetic water. The grown crystals are subjected to powder X-ray analysis, UV-Visible NIR and FTIR measurements.

Experimental Work

Copper sulfate pentahydrate powder supplied by [BDH Chemicals Ltd Poole England] with "minimum assay (ex Cu) 98.5%, maximum limits of impurities, Alkalis (sulphated) 0.5%, Chloride (Cl) 0.005%, Iron (Fe) 0.08%", is used to grow $CuSO_4.5H_2SO_4$ single crystals by slow evaporation method using double distilled water, diluted acid (H_2SO_4) and magnetic water as solvents. Copper sulfate pentahydrate powder is dissolved in 100 ml of, double distilled water, diluted H_2SO_4 acid and magnetized water to obtain (1 M). The solutions were stirred very well until homogeneous saturated solutions were obtained, and then the solutions were filtered using filter paper. The solutions were left to evaporate slowly at room temperature. Magnetic water is prepared from distilled water by putting the water between the poles of magnet for (3 hours). Figure (1) shows the magnet used in our study and the relation between magnetic field and the distance between the magnetic poles. The magnetic flux density is measured by "Gauss/Tesla meter NV621" made by (NVIS-Technology) and it is found to be (500 Gauss) in the center. The samples were prepared for measurement of UV-Visible by cutting and polishing them into plates of a thickness (2 mm), and for measurement of XRD and FTIR crushed to get the powder. The X-ray diffraction data for powder samples were recorded using "XRD 6000" made by "Shimadzu (Japan)" with CuKα target, wavelength (1.5406 Å), scan model continues scan, range (10-50) degrees. UV–Visible absorption spectra were recorded by using "UV–Visible 1800 Double beam spectrophotometer" made by "Shimadzu" in the range of (200-800 nm).

Results and Discussion

1. Crystal growth

Blue single crystals were obtained by spontaneous nucleation from the mother solution. The time of nucleation and the size of large crystals are shown in table (1), it was observed that the crystal grown from distilled water have long time for starting of nucleation as it compared with other solvent and its show the best result due to slow nucleation rate. If the nucleation is started in a single nucleus it will grow faster that than if there was of many nuclei [7]. The crystals grown using distilled water as a solvent had complete faces with tetrahedron shape, while the crystal for other solvents characterized by one of the incomplete faces. Photographs of the grown crystals are shown in the figure (2).

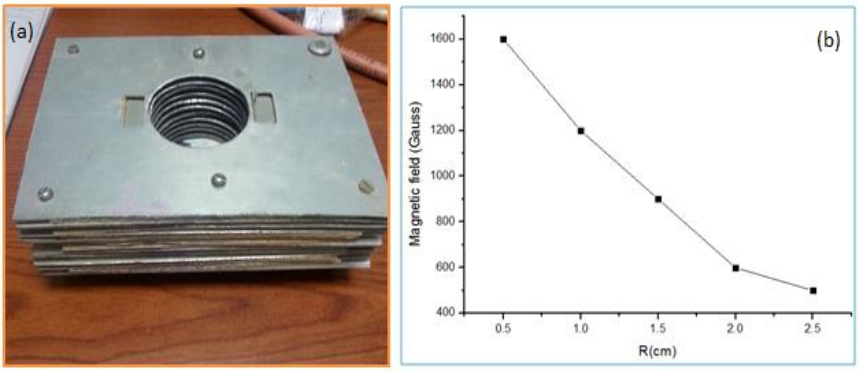

Fig. 1: (a) homemade magnetic arrangement used in the current study to prepare magnetic water. (b) The relation between magnetic field and the distance between the magnetic poles.

Table (1): Type of solvent, time of crystallization of grown crystals and size of large crystals obtained in this study.

Type of solvent	Time of starting of nucleation (days)	Time of completion of crystal (days)	Size of large crystal (mm^3)
Distilled water	55	57	21.6×19.38×3
H_2SO_4 acid	16	38	14.5×34.11×42.3
Magnetic water	25	37	42.4×27.36×7.5

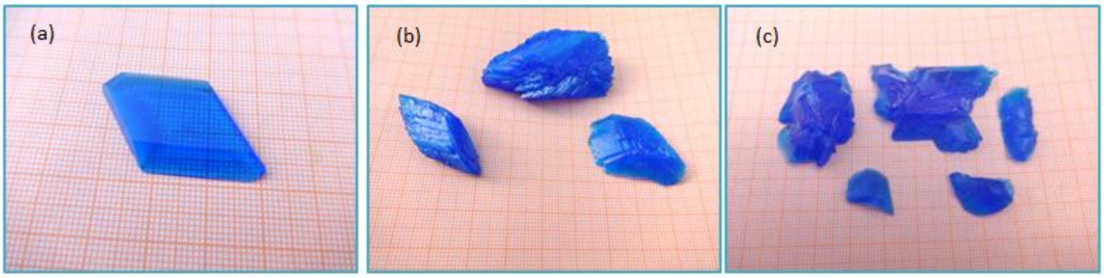

Fig. 2. Photographs of single crystals (a) Distilled water. (b) Diluted H_2SO_4 acid. (c) Magnetic water.

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 excess of anion SO_4. At low pH values, chemical impurities played the predominant role. Their entry into the growing crystal was increased with decreasing pH. The magnetic water did not improve 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) [6,8]. These results are attributed to faster proton transfer from H- ions to water molecules, due to proton spin inversion in the external field [9]. The magnetic field leads to reduction in surface tension of water [10], thus leads to decrease in the interfacial tension, which in turns increase the nucleation rate, so CSP precipitation increases [11,12]. This result is similar to the precipitation behavior of calcium carbonate ($CaCO_3$) as reported by Saksono et al. [13]. The crystal size depends on the rate of nucleation and its growth, whereas the morphology of a crystal is a result of altering the relative growth rates of the crystal faces [11].

2. Powder X-ray Diffraction (PXRD) Analysis

XRD pattern of the grown crystal are presented in figure (3) which shows that the crystals structure belongs to the triclinic system and the calculated parameters agrees with the "International Centre for Diffraction Data (ICDD)" card number 11-0646 as shown in table (2). The cell parameters are different from one sample to another depending on the solvent type. Their sharp peaks refer to good quality crystalline nature [14,15].

The highest peak appeared at 2θ~ 22° for the growth from distilled water, 2θ~ 31° for H_2SO_4 acid and 2θ~18° for magnetic water, which are refer to (011), $(1\bar{2}1)$ and $(0\bar{1}1)$ planes respectively, these differences due to shapes and colors of crystals [16].

The H_2SO_4 and the magnetic water causes increase in the intensity of peaks compared with the crystals grown by distilled water. This reveals that the acid has changed the tetrahedral SO_4 anion which is due to change in the S–O bond length and the bond lengths in sulfuric acid for S–OH.

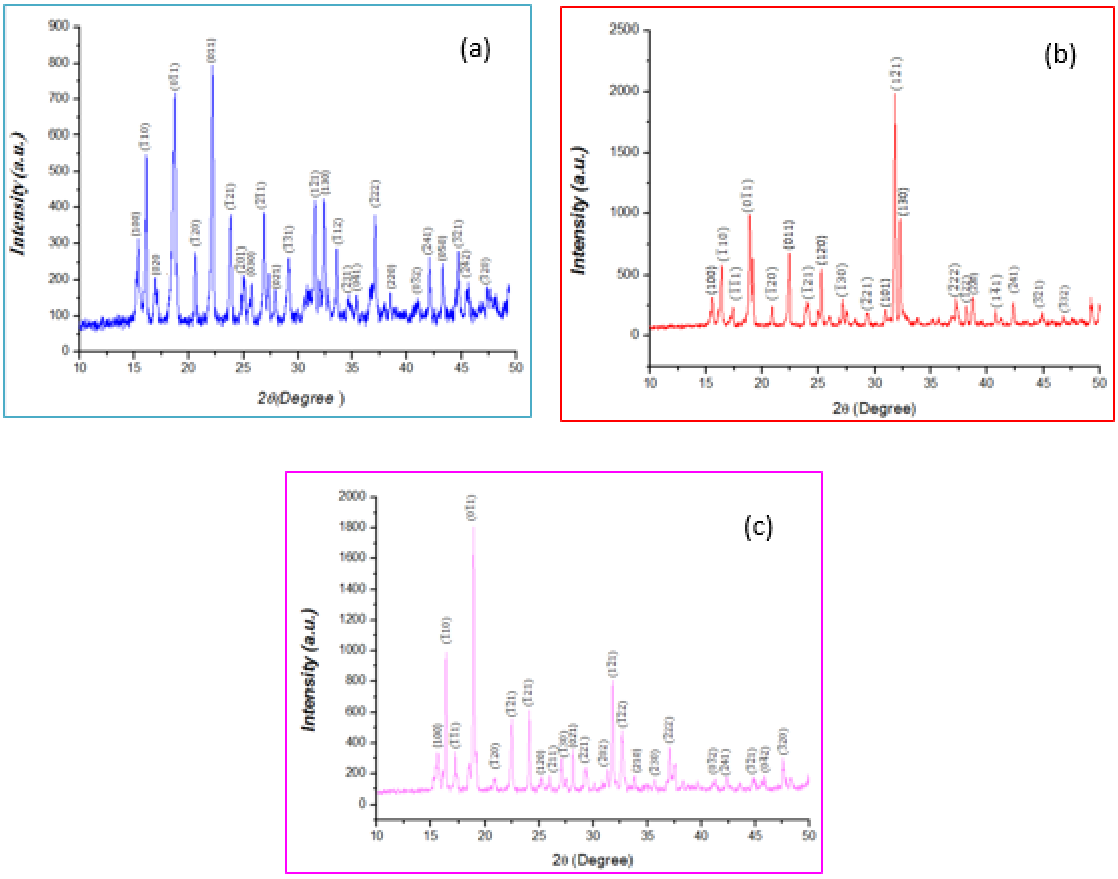

Fig. 3: PXRD patterns of grown crystal by (a) distilled water, (b) H_2SO_4 acid. (c) magnetic water as a solvent.

Table 2: Unit cell parameters for crystals grown using different solvent.

Unit cell parameter	distilled water	H_2SO_4 acid	magnetic water	Standard (11-0646)
a (Å)	7.168	7.202	7.239	7.155
b (Å)	10.69	10.85	10.686	10.71
c (Å)	5.941	5.956	5.995	5.955
α (deg.)	97.51	97.20	97.59	97.63
β (deg.)	125.5	125.3	126.289	125.3
γ (deg.)	94.39	94.41	94.525	94.32

3. Fourier Transform Infrared (FTIR) Analysis

The Fourier transform infrared spectra of CPS crystals from distilled water, H_2SO_4 acid and magnetic water were recorded in the range of (400-4000 cm^{-1}) are shown in Figure 4(a, b, c) The O-H stretching absorption bands appear at (3109 cm^{-1}, 3309 cm^{-1}, 3136 cm^{-1}) for crystal grown using distilled water, diluted acid and magnetic water as a solvent respectively [15,17]. Bending vibration of O-H appears at (1629 cm^{-1}) and (1672 cm^{-1}) for crystal grown using distilled water and magnetic water as a solvent [18]. Bending of S-O-H appears at (1539 cm^{-1} and 1577 cm^{-1}) for crystal grown by diluted acid and magnetic water [17]. The stretching vibration of S-O group appears at (1151 cm^{-1}, 1155 cm^{-1}, 1111 cm^{-1}) for crystal grown by distilled water, diluted acid and magnetic water as a solvent respectively. The Vibration mode of metal ion Cu^{+2} (Cu-O-H) appears at (887 cm^{-1}) for distilled water and at (879 cm^{-1}) for the magnetic water [15]. The metal ion Cu^{+2} disappears at crystal grown using H_2SO_4 acid because it may be contained hydrogen peroxide so that will have the oxidizing power to dissolve copper metal Cu^{+2}. The SO_4 degenerate mode appears at (659 cm^{-1}, 661 cm^{-1}, 621 cm^{-1}) for distilled water, diluted acid and magnetic water respectively [19]. The SO_4^{-2} bending group of sulfate appears at (482 cm^{-1}) for the crystal grown using distilled water as a solvent and at (443 cm^{-1}) for crystal grown using magnetic water [20].From above, it is found that the FTIR transmittance of crystals grown from H_2SO_4 acid is lower that from distilled water, and the FTIR transmittance of the crystals grown from magnetic water is lower than that of the crystal grown from distilled water and higher that of crystals grown from the H_2SO_4 acid. It is observed that the metal ion Cu^{+2} Cu-O-H appear in the crystals grown from distilled water and not appear in the crystals grown from H_2SO_4 acid and appearance with less intensity in the crystal from magnetic water.

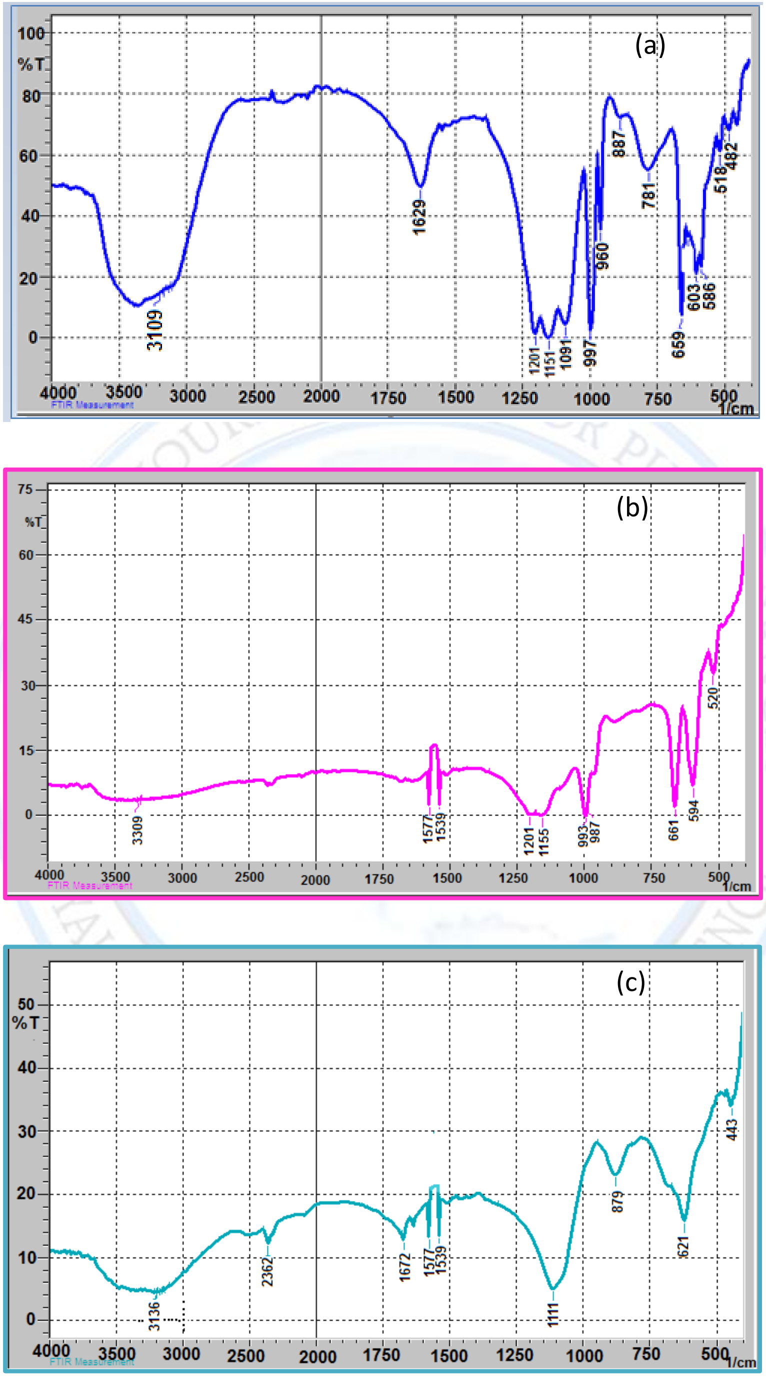

Fig. 4: FTIR transmission spectra of crystals grown using (a): Distilled water. (b): H_2SO_4 acid. (c): Magnetic water.

4. UV-Visible Spectral Analysis

Figure (5) shows the relation between transmittance and wavelength for single crystal of (CSP). The transmittance for all samples increases as the wavelength increases in the range of (275-470) nm, (277-487) nm and (275-470) nm, then decreases as the wavelength increases further. The cut-off wavelengths are shown in table (3). The spectra show high transmittance in the visible region but there is no transmittance in the infrared region, and low in the ultraviolet region, this is in agreement with the results reported by Anne et al. [15].

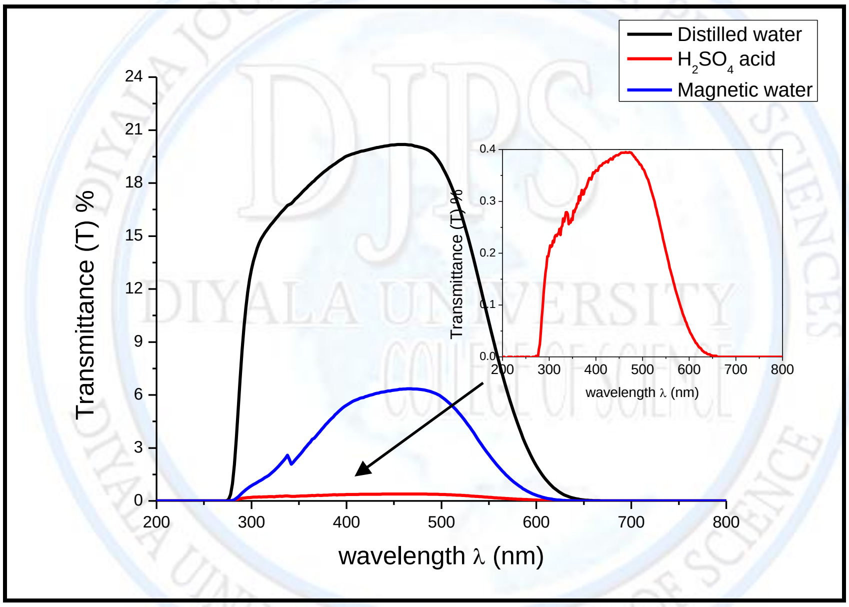

Fig. 5: Transmittance (T) versus wavelength (λ) of CSP single crystals grown using different solvents.

The crystal grown using distilled water has a maximum transmittance of nearly equal to (20.1%) at the wavelength of (446 nm). It is transparent in the wavelength range between (300 nm) and (530 nm), so it can be used as optical band pass filters for this range, this result is in agreement with the results reported by Anne et al. and Manomenova et al. [15,23]. The crystals grown by H_2SO_4 acid and magnetic water are transparent in the wavelength range of (311-497) nm and (307-523) nm respectively. A graph between $(\alpha h\nu)^{1/2}$ and $(h\nu)$ are presented in figure (6), a straight line is obtained which gives the value of the indirect band gap. The extrapolation of the straight line to $(\alpha h\nu)^{1/2} = 0$ gives the energy gap for all the grown crystals grown are shown in table (3).

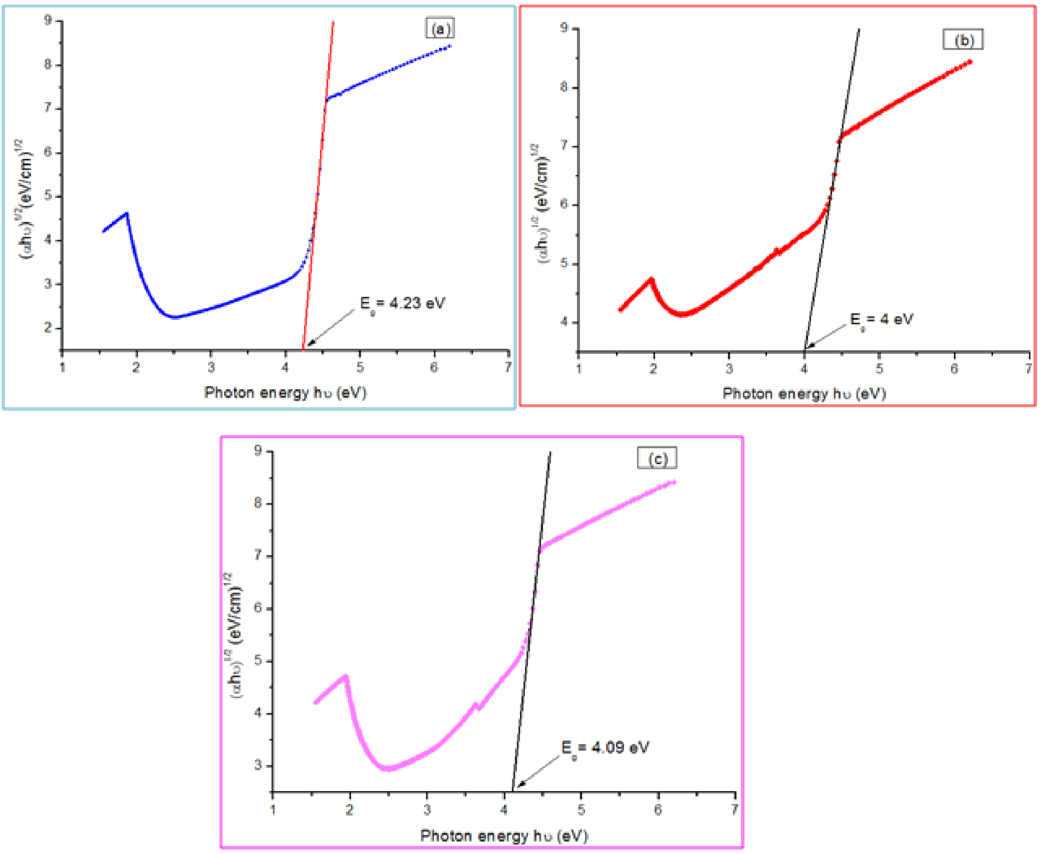

Fig. 6: The relation between $(\alpha h\upsilon)^{1/2}$ and $(h\upsilon)$ of single crystal grown using (a): Distilled water. (b) H_2SO_4 acid. (c) Magnetic water.

Table 3: Cut-off wavelength and energy gap of single crystals grown using different solvent.

Solvent	E_g (eV)	Cut-off wavelength (nm)
Distilled water	4.23	280
H_2SO_4 acid	4	292
Magnetic water	4.09	287

Conclusions

The technique of slow evaporation for solution of $CuSO_4.5H_2O$ is suitable for grown crystals at room temperature. The distilled water led to grow best crystal because it have best time to grow was (57 days) and have best shape. The magnetic water did not improve the morphology of crystal because the (CSP) is paramagnetic material. The XRD analysis confirms that the crystalline system for crystals (CSP) is triclinic. From the FTIR it is observed that the metal ion Cu^{+2} appear in the crystals grown using distilled water and disappear in the crystals grown using H_2SO_4 acid and appearance with less intensity in the crystal grown using magnetic water. From UV-Visible spectra, it was found the H_2SO_4 acid causes to decrease the transmittance and the energy gap, and it is noted the magnetic water causes to decreases the transmittance and energy gap but by lower rate. The crystals can be used as optical band pass filters between the range (~300 nm) and (600 nm). The best condition of grow crystal was be (temperature constant and pressure constant and slow evaporation and used distilled water as solvent).

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