

Synthesis and Characterization of Potassium Copper Sulphate Hydrate Nanoparticles

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Abstract

Nanoparticles of potassium copper sulphate hydrate $K_2[(CuSO_4).(H_2O)_6]$ were prepared using co-precipitation method. Brown coloured precipitate was obtained. The nanoparticle so obtained was characterized by powder X-ray diffraction, Fourier Transform Infrared Spectroscopy, Ultra-violet spectroscopy and Scanning Electron Microscope techniques. The d-spacing and 2-Theta values from XRD were compared with JCPDS values. The average grain size of potassium copper sulphate hydrate nanoparticles were confirmed to be 27.70 nm from XRD according to the Debye-Scherrer's formula. The stretching and bending frequencies of various molecular functional groups are studied from FT-IR spectrum. The SEM image shows well crystallized particles with flake like morphology. UV-Visible spectrum is used to determine the band gap of the sample.

Keywords: Potassium Copper Sulphate Hydrate, XRD, FT-IR, UV-Visible Spectroscopy, SEM.

1. Introduction

Nanometer sized particles display many interesting optical, electronic, magnetic and chemical properties yielding applications in biological nano sensors, optoelectronics, nano devices, nano electronics, information storage and catalysis [1, 2]. Amongst many metals like Au, Ag, Pd, Pt, towards which research is directed, copper and copper based compounds are the most important materials. The metallic Cu plays a significant role in modern electronics circuits due to its excellent electrical conductivity and low cost nanoparticles [1, 3]. In this work, potassium copper sulphate hydrate nanoparticles were prepared and their structural and optical properties were studied.

2. Experimental Details

Potassium copper sulphate hydrate (PCSH) nanoparticles were synthesized by adding copper sulphate pentahydrate and potassium chromate using co-precipitation method. Precise amounts of reagents taking into account their purity were weighed and dissolved separately in distilled

water into 0.2M concentration. After obtaining a homogeneous solution, the reagents were mixed using magnetic stirring. The precipitate was separated from the reaction mixture and washed several times with distilled water. The wet precipitate was dried and thoroughly ground using agate mortar to obtain the samples in the form of fine powder.

3. Results and Discussion

3.1 XRD-Particle size determination

Powder X-ray diffraction is an ideal technique for the determination of crystallite size of the powder samples. The basic principle for such a determination involves precise quantification of the broadening of the peaks. The size of the synthesized potassium copper sulphate hydrate nanoparticles are calculated using Scherrer equation

$$D = 0.9 \lambda / \beta \cos \theta$$

where λ represents wavelength of X rays, β represents half width at full maximum and θ is the diffraction angle. The average grain size of the particles is found to be 27.70 nm. The XRD pattern of potassium copper sulphate hydrate nanoparticles is shown in fig.1.

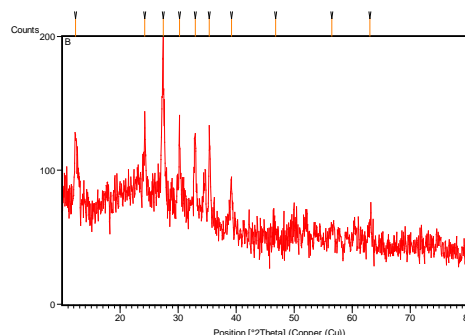


Fig.1. XRD pattern of PCSH nanoparticles

A good agreement between the experimental diffraction angle [2 θ] of the specimen and its standard diffraction

angle [2θ] is confirming standard of the specimen. The peaks at 2θ values of the sample are observed and tabulated in table-1. It is compared with the standard powder diffraction card of Joint Committee on Powder Diffraction Standards (JCPDS), corresponding to potassium copper sulphate hydrate file No. 86-0760. The d-spacing values of experiment are also confirming to the standard values.

Table-1. Experimental and standard diffraction angles of PCSH nanoparticles

Experiment		Standard JCPDS (86-0760)	
Diffraction angle(deg)	D-spacing(Å)	Diffraction angle(deg)	D-spacing(Å)
12.3223	7.1831	12.501	7.0748
24.2580	3.6691	24.411	3.6434
27.4077	3.2542	27.357	3.2574
30.2283	2.9566	30.237	2.9534
32.9523	2.7182	32.932	2.7176
35.3933	2.5361	35.374	2.5354
39.2226	2.2969	39.255	2.2932
46.7663	1.9425	46.839	1.9380
56.4937	1.6289	56.560	1.6258
63.0722	1.4739	63.094	1.4723

3.2 XRD-Dislocation density

The dislocation density is defined as the length of dislocation lines per unit volume of the crystal. In material science, a dislocation is a crystallographic defect, or irregularity, within a crystal structure. The presence of dislocations strongly influences many of the properties of materials. The movement of a dislocation is impeded by other dislocations present in the sample. Thus, a larger dislocation density implies a larger hardness. The X-ray line profile analysis has been used to determine the dislocation density.

The dislocation density can be calculated from the relation

$$\delta = \frac{1}{D^2}$$

Where δ is dislocation density and D is the crystallite size. The dislocation density calculated from formula is given in table-2.

The number of unit cells in the crystallite can be expressed as

$$N = \pi (4/3) \times (D/2)^3 \times (1/V)$$

Where D is the crystallite size and V is the cell volume of the sample.

Table-2. Dislocation density and Number of unit cells of PCSH nanoparticles

Pos.[2θ] (Degree)	Particle size (nm)	Dislocation density (m ⁻²)	Number of unit cells
12.3223	20.29	2.4290 x10 ¹⁵	0.0678 x10 ⁵
24.2580	20.64	2.3474 x10 ¹⁵	0.0714 x10 ⁵
27.4077	27.70	1.3033 x10 ¹⁵	0.1727 x10 ⁵
30.2283	55.86	3.2048 x10 ¹⁴	1.4166 x10 ⁵
32.9523	33.69	8.8104 x10 ¹⁴	0.3107 x10 ⁵
35.3933	33.91	8.6965 x10 ¹⁴	0.3169 x10 ⁵
39.2226	28.57	1.2251 x10 ¹⁵	0.1895 x10 ⁵
46.7663	8.79	1.2943 x10 ¹⁶	0.0055 x10 ⁵
56.4937	7.64	1.7132 x10 ¹⁶	0.0036 x10 ⁵
63.0722	15.79	4.0108 x10 ¹⁵	0.0319 x10 ⁵

It is observed from these tabulated details, and from figures. 2, 3 & 4 the dislocation density is inversely proportional to particle size and number of unit cells. Dislocation density increases while both particle size and number of unit cells decrease [4].

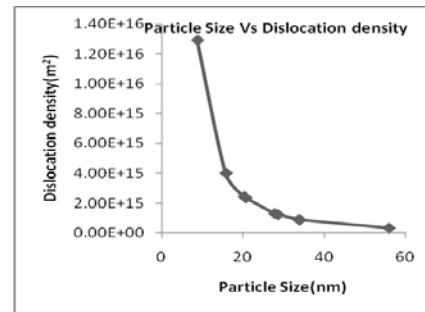


Fig.2. Dislocation density Vs Particle size for PCSH nanoparticles

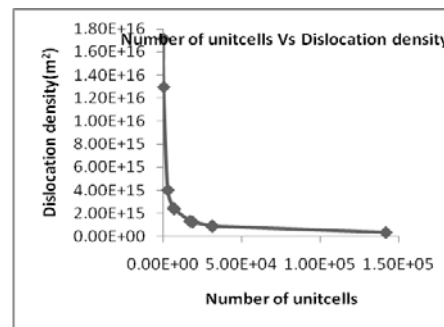


Fig.3. Number of Unit cells Vs Dislocation density for PCSH nanoparticles

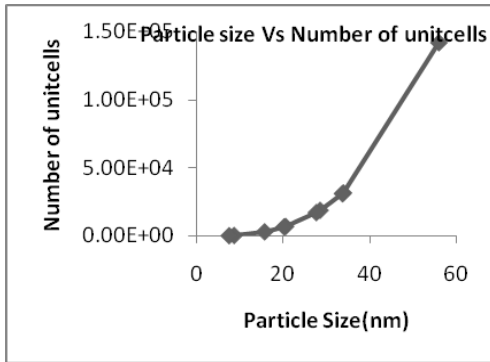


Fig.4. Particle size Vs number of unit cells for PCSH nanoparticles

3.3 XRD-Morphology Index

The morphology index (MI) is found from FWHM of XRD data using the equation

$$MI = \frac{FWHM_h}{FWHM_p + FWHM_h}$$

Where M.I. is morphology index, $FWHM_h$ is highest FWHM value obtained from peaks and $FWHM_p$ is value of particular peak's FWHM for which M.I. is to be calculated. The relation between particle size and morphology index are shown in table-3.

Table-3. Morphology Index and Particle size of PCSH nanoparticles

FWHM (β) (radian)	Particle size (nm)	Morphology Index
0.00687	20.29	0.4285
0.00687	20.64	0.4285
0.00515	27.70	0.5000
0.00257	55.86	0.6671
0.00429	33.69	0.5456
0.00429	33.91	0.5456
0.00515	28.57	0.5000
0.01717	8.79	0.2307
0.02059	7.64	0.2001
0.01030	15.79	0.3333

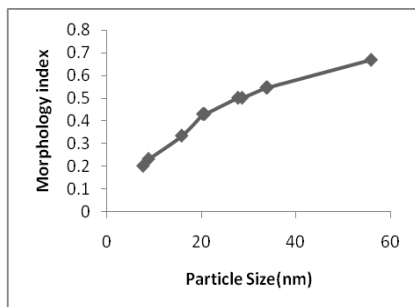


Fig.5. Particle size Vs Morphology Index of PCSH nanoparticles

It is observed that morphology index has direct relationship with particle size and the results are shown in Fig.5.

3.4 XRD-Unit cell parameters

Unit cell parameter values calculated from XRD are enumerated in table-4.

Table-4. XRD Parameters of PCSH nanoparticles

Parameter	Value
Structure	Primitive
Space group	P2 ₁ /a
Symmetry of lattice	Monoclinic
Particle size	27.70 nm
Lattice parameters	a = 9.03Å, b = 12.022Å c = 6.121Å
Lattice angle	$\alpha = \gamma = 90^\circ, \beta = 104^\circ$
Volume of unit cell(V)	643.93 Å ³
Density (\bar{n})	2.279 g/cm ³
Dislocation density	1.3033 x 10 ¹⁵ m ⁻²
Mass	441.95 amu

4. FTIR Studies

The FTIR spectrum of the potassium copper sulphate hydrate is shown in the fig.6. The FTIR spectrum shows a peak at 617 cm⁻¹ is due to the Cu-O stretching bond and the peak at 896 cm⁻¹ are due to presence of Cu-OH stretching bond. The peaks at 3769 cm⁻¹, 3871 cm⁻¹ corresponding to the free O-H stretching vibration and the peak at 1636 cm⁻¹ is bending mode of hydroxyl group. The peak at 957 cm⁻¹ indicating S=O double stretching bond vibration.

The peaks at 881 cm⁻¹ and 613 cm⁻¹ indicating Cu-OH stretching vibration and Cu-O stretching bond [5-7] respectively. This region is very different from pure water and water cluster frequency ranges 3600-3800 cm⁻¹ for O-H stretches and 1600 cm⁻¹ for HOH bends. The infrared intensities of these vibrations are about 20-30 times higher than those of the strongest pure water O-H vibrations [8]. The S=O stretching vibration occurs between the regions 1009 to 935 cm⁻¹ [8].

The sulphate ions have a T_d symmetry in the free state with its vibrational modes distributed as $\Gamma_{vib} = A_1(\nu_1) + E(\nu_2) + 2F_2(\nu_3 + \nu_4)$. The modes ν_1 and ν_3 are labeled as the bond stretching and ν_2 and ν_4 are mostly as the bending modes in the usual approximation. The A₁ species is singly degenerate, E is doubly degenerate and F₂ species have

triply degenerated. The wavenumbers of the fundamental transition are well known, $\nu_1(A_1)=983\text{cm}^{-1}$, $\nu_2(E)=450\text{cm}^{-1}$, $\nu_3(F_2)=1105\text{cm}^{-1}$, $\nu_4(F_2)=611\text{cm}^{-1}$ [9]. The symmetric stretching mode of $\nu_1 = 957\text{cm}^{-1}$ is observed in IR spectrum. The frequency ν_2 appears at 452cm^{-1} in the IR spectrum for symmetric bending mode of $(\text{SO}_4)^{2-}$ ion. The antisymmetric stretching mode ν_3 is found to occur at 1113cm^{-1} and antisymmetric bending vibration ν_4 is observed at 617cm^{-1} in the IR spectrum.

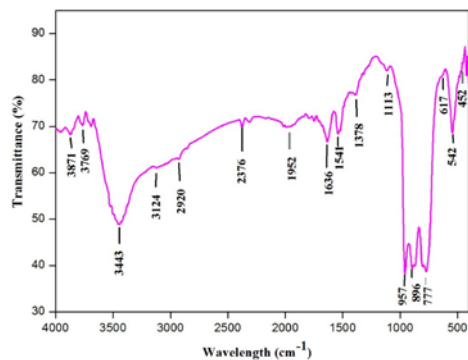


Fig.6.FTIR spectra of PCSH nanoparticles

5. SEM studies

The size and morphology of potassium copper sulphate hydrate nano particles are analysed using scanning electron microscopy. The SEM images of potassium copper sulphate hydrate nano-particles are shown in Fig.7 at various magnifications. In SEM, most of the particles have flake like morphology. In this case the particles sizes are slightly increased and is also observed that the particles are distributed with agglomeration.

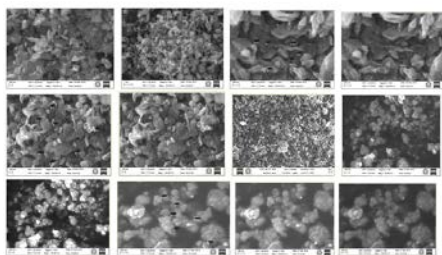
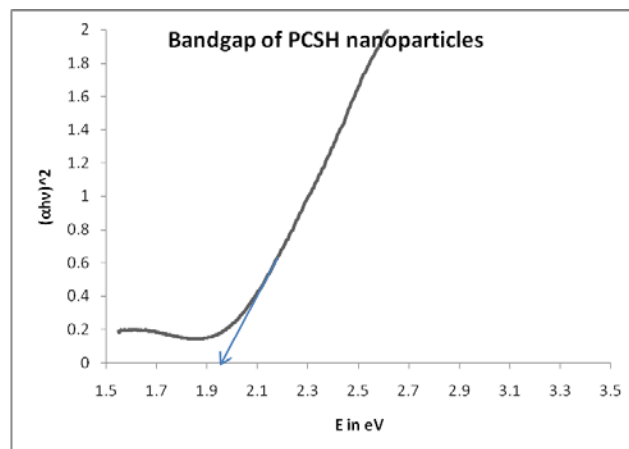


Fig.7. SEM images of PCSH nanoparticles at various magnifications

6. UV Studies

The band gap of the prepared sample PCSH nanoparticles were determined by using UV visible studies. From the UV spectrum the optical band gap of PCSH nanoparticles was

found to be 1.95eV . Fig.8 shows the graph to find the band gap of PCSH nanoparticles.



7. Conclusions

The PCSH nanoparticles have been prepared by chemical co-precipitation method. XRD analysis suggests that the average particle size is in the nano range of the order of 27.70nm . The SEM picture reveals the well crystallized particles with flake like morphology. From the FTIR spectrum, the stretching and bending frequencies of the molecular functional groups in the sample were identified. From the UV spectra, the band gap was found to be 1.95eV .

8. References

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