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Growth, Structural and Optical characteristics of Citric Acid Doped Copper Sulphate Single Crystals Polymer Composites Photonic Applications

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Abstract

The organic material Citric Acid doped Copper Sulphate single crystals (CACS) was synthesized and single crystal was grown by slow evaporation method. The incorporation of citric acid, an organic compound, introduces polymer-like functional behavior into the crystal matrix, forming an organic-inorganic hybrid composite with enhanced optical and structural characteristics. Single crystal XRD confirmed the triclinic system with unit cell parameters: a = 5.96 Å, b = 6.11 Å, c = 10.74 Å, and angles α = 77.14°, β = 82.34°, γ = 72.64°. Powder XRD analysis displayed sharp peaks, indicating high crystallinity. FTIR spectra confirmed the presence of functional groups such as –OH and SO_4^{2-}*, validating the successful interaction of citric acid with the copper sulfate lattice and suggesting hydrogen bonding and molecular-level integration—features commonly seen in polymer-based systems.*

Optical transparency studies using UV-Vis spectroscopy revealed a cut-off wavelength at 350 nm and a band gap of 3.55 eV, indicating excellent nonlinear optical (NLO) properties. The second harmonic generation (SHG) efficiency was tested using the Kurtz powder technique, and a high laser damage threshold (LDT) of 2.32 GW/cm² was observed—superior to that of standard materials like KDP. These results highlight the promise of CACS as a polymer-influenced hybrid composite material for photonic and optoelectronic applications, especially in environments demanding high optical clarity and laser durability. This study contributes to the growing interest in organic-inorganic composite crystals for next-generation NLO devices.

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INTRODUCTION

In recent years, optical materials have played a dominant role in the electronics industry for the development of efficient optoelectronic devices. The characterization of nonlinear single crystals with enhanced physicochemical properties has become highly valuable in designing components for photonic and optoelectronic applications. These nonlinear effects are crucial in advanced technologies such as frequency doubling, optical switching, quantum communication, and data storage, leading to increased interest in nonlinear materials [1–3].

Organic single crystals are a fascinating class of materials for nonlinear optical (NLO) applications due to their high nonlinear susceptibilities, fast response times, lightweight nature, and flexible molecular structures. Compared to inorganic crystals, organic materials can often be tailored at the molecular level for specific optical functions. Semi-organic crystals represent a hybrid class of NLO materials, offering the high nonlinear response of organic systems with the thermal and mechanical stability typical of inorganics making them particularly attractive for photonic applications [4–6].

In the context of modern materials science, these semi-organic compounds can also be classified as polymer-influenced hybrid composites, especially when organic dopants like citric acid integrate with inorganic salt matrices. Such combinations often result in molecular-level composites where hydrogen bonding and ionic interactions mimic polymer-like behavior. This class of functional crystalline composites bridges the gap between organic polymers and crystalline solids, offering multifunctional properties for emerging optoelectronic applications.

Organic materials possess excellent optical characteristics, which are vital in device fabrication. As a result, researchers are increasingly encouraged to develop new nonlinear materials with strong optical performance. Therefore, organic and inorganic hybrid material was grown via the slow solvent evaporation method, and several characterizations were carried out to demonstrate its significant nonlinear characteristics and inherent physicochemical nature for intensive photonic applications [7, 8].

Citric acid (an organic acid) is widely used in the food, pharmaceutical, and chemical industries. Its salts, formed by combination with other compounds, lead to hydrogen-bonded molecular structures, which have been extensively studied using X-ray and spectroscopic techniques [9–11]. Citric acid exists in both anhydrous and monohydrate forms, which differ in solubility and crystal packing arrangements [12].

Copper sulfate pentahydrate is an important industrial compound related to copper mining and is extensively used in commercial applications [13–15]. Crystallization studies of copper sulfate pentahydrate in the absence and presence of sodium chloride were previously reported [16]. The citric acid-doped copper sulfate single crystal exhibits improved NLO activity and thermal stability due to the synergistic interaction between the organic and inorganic components.

The resulting material can be considered a novel organic-inorganic composite system, where the doping process leads to internal structural modifications that enhance both optical and mechanical behavior. This hybrid nature aligns with the core focus of polymer composite research, where functionality arises from the interplay of soft and hard material phases.

The colorful copper sulfate crystal has diverse industrial uses ranging from synthetic fiber production to applications in electrolytic copper refining, anti-fouling paint formulations, glass coloring, and as an antiseptic and antifungal agent. Growth and characterization of copper sulfate pentahydrate crystals were investigated [17], while copper sulfate crystallization in freshwater was explored [18], and by Zumstein and Rosseau [19] in their studies on agglomeration during continuous crystallization.

Copper sulfate doped with various organic acids and amino acids has been widely reported due to its high optical efficiency. Recently, Huda I. Ahmed *et al.* [20] synthesized and characterized copper sulfate single crystals, while L-histidine-doped copper sulfate single crystals were reported by Mary Depheine *et al*., and copper guanidinium sulfate single crystals by P. Christuraj *et al*., confirming their suitability as SHG nonlinear materials in optical device fabrication.

Hence, we report the growth and characterization of a citric acid-doped copper sulfate pentahydrate single crystal to demonstrate its exceptional potential in nonlinear optical applications, with notable NLO efficiency, making it a promising polymer-influenced composite material for next-generation photonic devices.

MATERIAL SYNTHESIS

A highly transparent blue colour citric acid doped copper sulphate pentahydrate single crystals is grown by slow evaporation method. Citric acid with 0.02 mol % is added to copper sulphate solution is stirred using a magnetic stirrer at 35^0C for 5 hours to obtain limpid solution is as shown in figure 1. The solution is filtered using whatmann filter paper and is transferred in a beaker and covered with a thin transparent sheet and kept for crystallisation.

After a course of 25 days a colorful transparent single crystal were grown and the image is shown in Figure 2.

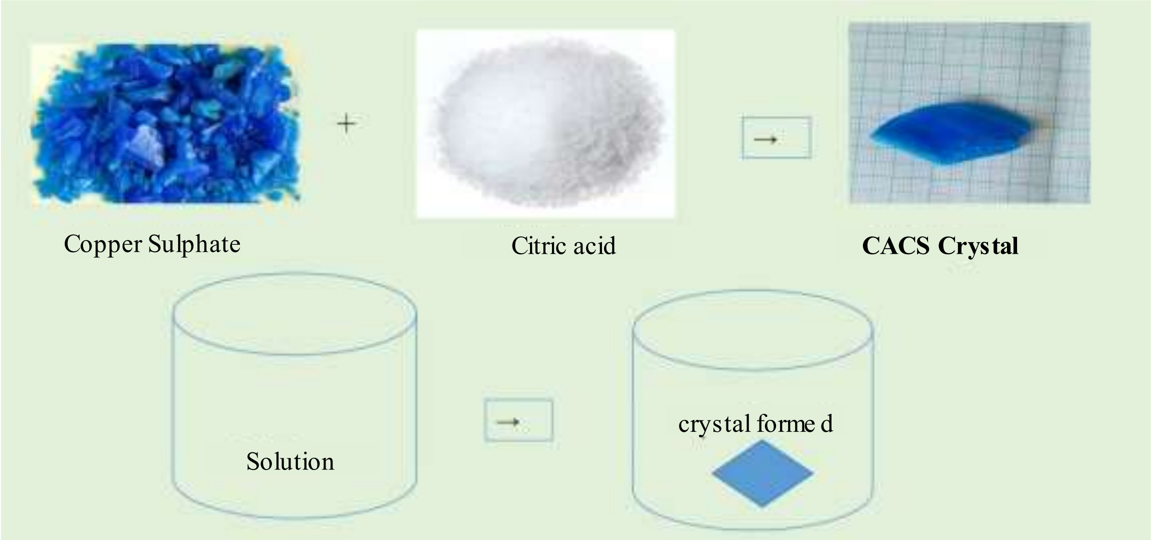

Figure 1. Synthesis Process

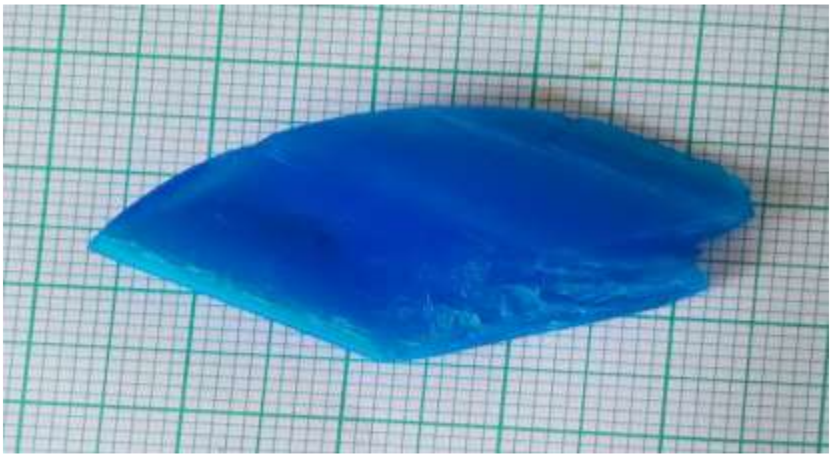

Figure 2. Photograph of CACS Crystal

CHARACTERIZATION TECHNIQUES

The investigation is executed by BRUKER KAPPA APEX II CCD diffractometer to find the crystal system and cell parameters for citric acid doped copper sulphate pentahydrate single crystal. Powder XRD data was recorded on an X-ray diffractometer in the range $2\theta=5^\circ$ - 90° using CuKα radiation of wavelength 1.5404 Å. Fourier Transform Infrared Spectral analysis is the widely used techniques to analyse the structure of the sample. The optical transmittance and absorbance spectrum is recorded for the grown material in the range from 300–800 nm with PERKIN ELMER LAMADA spectrophotometer. Nd: YAG laser beam with a wavelength of 1064 nm is used for analysing the second harmonic generation study employing Kurtz and Perry's method for the grown crystal.

Single Crystal XRD

The investigation is executed by BRUKER KAPPA APEX II CCD diffractometer to find the crystal system and cell parameters for citric acid doped copper sulphate pentahydrate single crystal. The conventional cell parameters obtained are (a, b, c) 5.96 Å, 6.11 Å, and 10.74 Å, and (α, β, γ) 77.14A°, 82.34 A°, 72.64 A° respectively, with a crystal system of Triclinic. The defined unit cell parameters are in good occurrence with the reported literature value [16, 17]. The crystallographic data for citric acid doped copper sulphate pentahydrate single crystal is presented figure 3.

Powder XRD

Powder XRD data was recorded on an X-ray diffractometer in the range 2θ = 5˚ - 90˚ using CuKα radiation of wavelength 1.5404 Å. The indexed powder XRD pattern is shown in figure. 4. High intensity peaks which are characteristics of the materials are present in the spectrum. It implies the good crystalline nature of the grown material.

FTIR

Fourier Transform Infrared Spectral analysis is the widely used techniques to analyse the structure of the sample. The powdered material was examined by FTIR techniques utilising Perkin Elmer Spectrophotometer in 4000 cm^{-1} to 500 cm^{-1} wave number and the spectra is given in figure 5. Absorption band at 3100 cm^{-1} represents the stretching vibration of OH group. The bending vibration of OH group is observed at 1667 cm^{-1}. The bending and stretching vibration mode of S-O group is assigned at the peak 601 cm^{-1} and 1066 cm^{-1} [21, 22]. Thus, the functional groups correspond to the vibrational assignments confirms the presence of the grown material.

UV Studies

The optical transmittance and absorbance spectrum is recorded for the grown material in the range from 300 – 800 nm with PERKIN ELMER LAMADA spectrophotometer.

The importance of this characterization is to show the transmission width and cut off wavelength. The nonlinear material should have the cut off wavelength ranging from 200–1600 nm. Figure 6 represents the UV absorption spectrum of the grown material, which predicts the cut off wavelength as 350 nm. The low absorbance with well high transmittance represents its efficiency over nonlinear properties. Overall, based on the cut off wavelength its energy band gap is calculated to be 3.55 eV. The more transmittance and broad energy gap shows low defect concentration in the grown material, shows its better possibility in photonic applications [23].

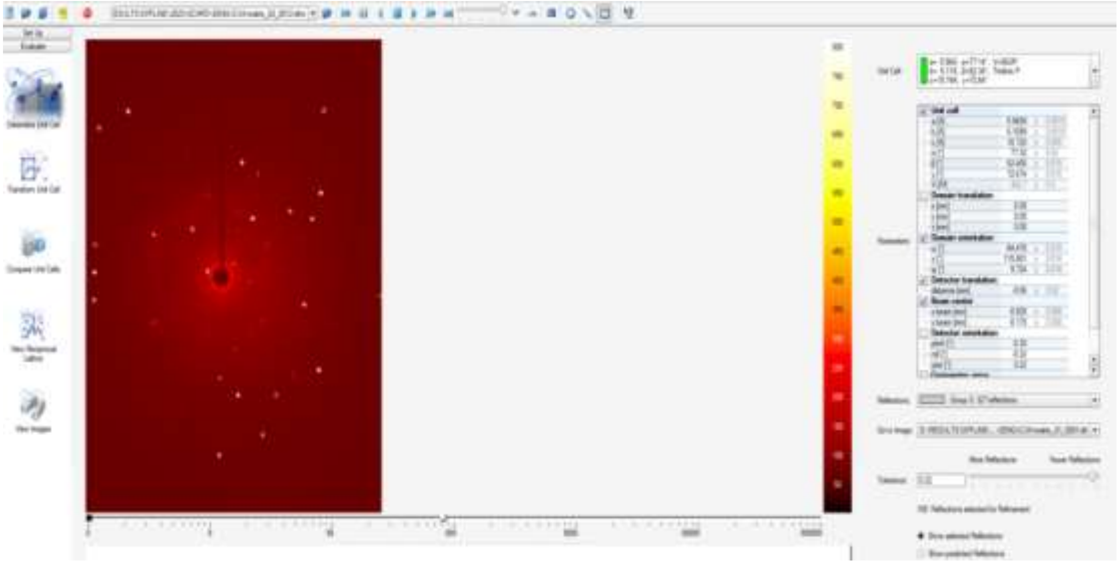

Figure 3. Crystallographic data of CACS Crystal

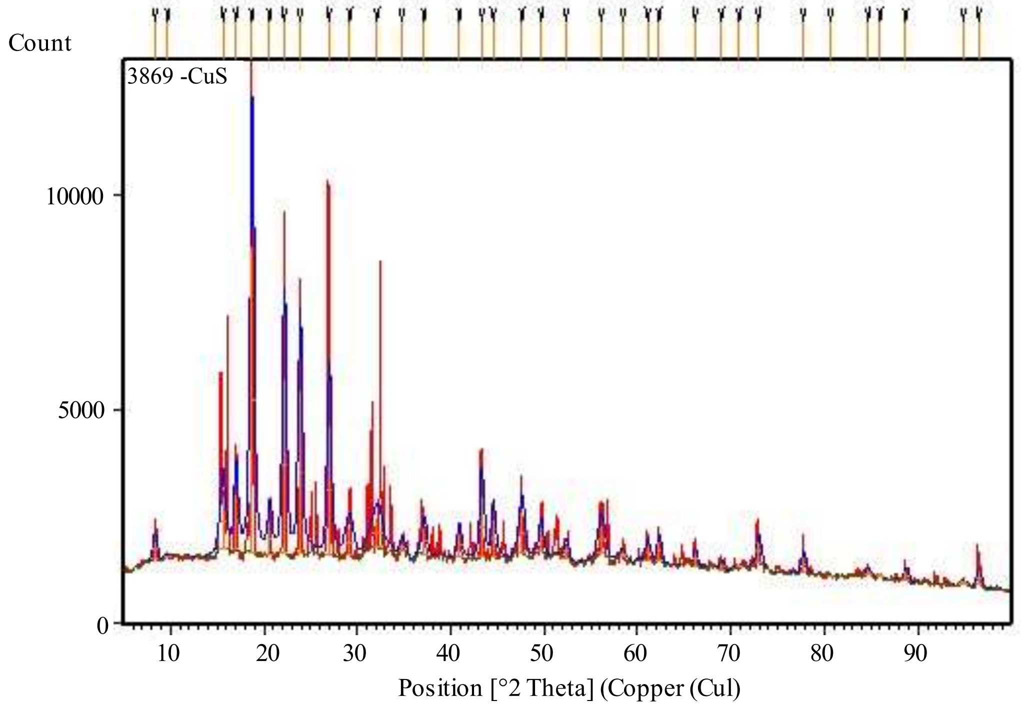

Figure 4. Powdered XRD of CACS Crystal

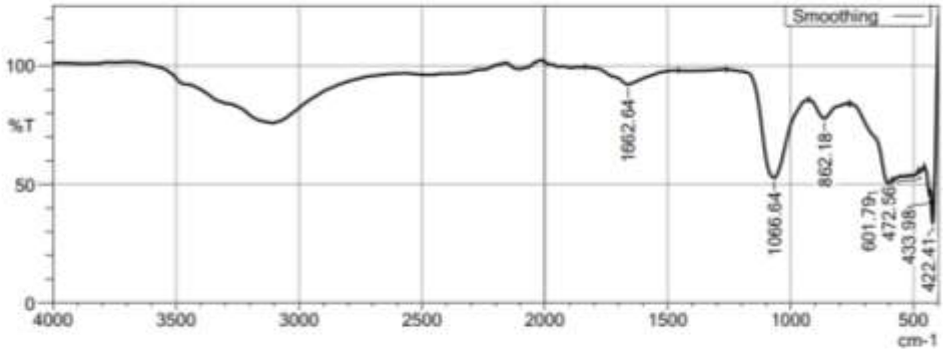

Figure 5. FTIR Spectra of CACS Crystal

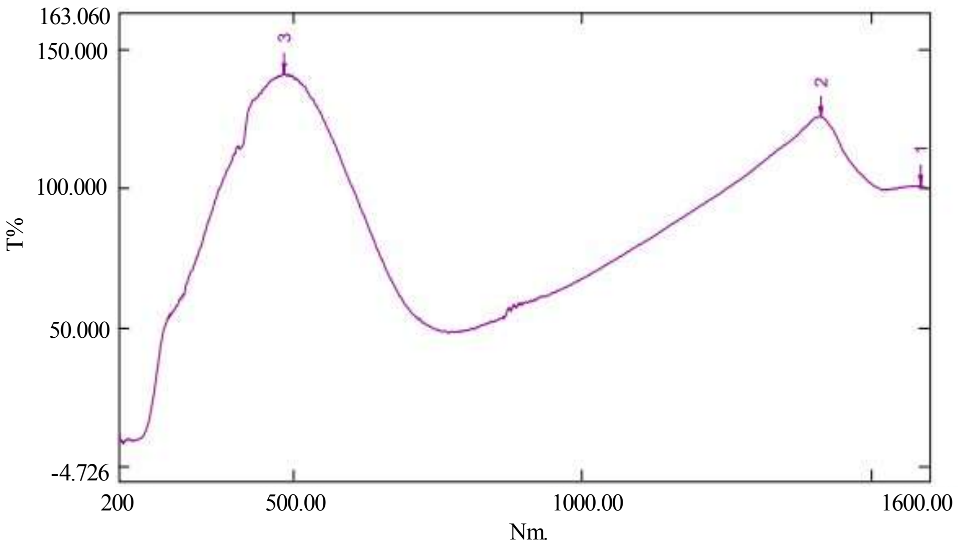

Figure 6. FTIR Spectra of CACS Crystal

SHG

Nd: YAG laser beam with a wavelength of 1064 nm is used for analysing the second harmonic generation study employing Kurtz and Perry's method for the grown crystal. The NLO efficiency was compared with the standard micro particles of KDP single crystals [24]. The feeble green light emission from the samples confirms the NLO property of the grown material.

Laser Damage Threshold

CACS single crystal undergoes LDT analysis, to show the withstanding capability of the material towards high power laser both linearly and nonlinearly. The LDT for CACS was estimated using power density equation [23].

$$\text{Power density } (P_d) = E / \tau\pi r^2 \ (\text{GW/cm}^2)$$

Where, input energy is E, pulse width is τ, radius of beam r. The LDT was 2.32 GW/cm^2 that has a larger value than KDP, Urea, authenticates its aptness in formulating laser based device.

CONCLUSION

An organic optical single crystal, citric acid-doped copper sulphate (CACS), was successfully grown and harvested over a period of 25 days using the slow solvent evaporation method. The single crystal X-ray diffraction data confirms that the grown crystal belongs to the triclinic system. The lattice parameters obtained from single crystal XRD analysis further validate the crystal structure, while powder XRD patterns reveal the well-defined crystalline nature of the material.The recorded FT-IR spectrum of the grown crystal confirms the presence of key functional groups, indicating the successful incorporation of citric acid into the copper sulphate matrix. The UV-VIS transmission spectrum demonstrates excellent optical transparency, and the observed cut-off wavelength highlights its potential in nonlinear optical applications. CACS exhibits a higher laser damage threshold (LDT) value compared to other conventional NLO single crystals, indicating improved thermal and optical endurance. The second harmonic generation (SHG) efficiency of the crystal was also evaluated, confirming its nonlinear optical activity.

The interaction between the organic dopant (citric acid) and the inorganic host lattice forms a semi-organic crystalline system that behaves as a molecular-level composite material. This type of hybrid structure mirrors certain polymer-composite characteristics—where the combination of soft organic components and hard inorganic phases leads to multifunctional behavior. The enhanced properties displayed by the CACS single crystal substantiate its suitability for use in optoelectronic devices, especially in fields demanding robust, composite-inspired optical materials.

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