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Research Article

Effect of Metal Dopant on Ninhydrin—Organic Nonlinear Optical Single Crystals

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In the present work, metal (Cu^{2+})-substituted ninhydrin single crystals were grown by slow evaporation method. The grown crystals have been subjected to single crystal XRD, powder X-ray diffraction, FTIR, dielectric and SHG studies. Single crystal X-ray diffraction analysis reveals that the compound crystallizes in monoclinic system with noncentrosymmetric space group P21 with lattice parameters $a = 11.28$ Å, $b = 5.98$ Å, $c = 5.71$ Å, $\alpha = 90^\circ$, $\beta = 98.57$, $\gamma = 90^\circ$, and $V = 381$ (Å)^3, which agrees very well with the reported value. The sharp and strong peaks in the powder X-ray diffraction pattern confirm the good crystallinity of the grown crystals. The presence of dopants marginally altered the lattice parameters without affecting the basic structure of the crystal. The UV-Vis transmittance spectrum shows that the crystal has a good optical transmittance in the entire visible region with lower cutoff wavelength 314 nm. The vibrational frequencies of various functional groups in the crystals have been derived from FT-IR analysis. Based on the shifts in the vibrations, the presence of copper in the lattice of the grown crystal is clearly established from the pure ninhydrin crystals. Both dielectric constant and dielectric loss decrease with the increase in frequency. The second harmonic generation efficiency was measured by employing powder Kurtz method.

1. Introduction

The search for new materials with high optical nonlinearity is an important area due to their practical applications such as optical communication, optical computing, optical information processing, optical disk data storage, laser fusion reactions, laser remote sensing, colour display, medical diagnostics, and so forth [1–4]. In semiorganic materials, the organic ligand is ionically bonded with inorganic host. Due to this, the new semiorganic crystals have higher mechanical strength and chemical stability. Most of the organic NLO crystals usually have poor mechanical and thermal properties and are susceptible to damage during processing even though they have large NLO efficiency. Also it is difficult to grow larger size optical quality crystals of these materials for device applications. Purely inorganic NLO materials have excellent mechanical and thermal properties but possess relatively modest optical non linearity because of the lack of extended pi-electron delocalization.

Organic NLO materials are often superior to inorganic in terms of their response speed, optical clarity, and the magnitude of their third order susceptibility and for a material to exhibit NLO activity it should be noncentro symmetric. Hence it may be useful to prepare semiorganic crystals which combine the positive aspects of organic and inorganic materials resulting in useful non linear optical properties. Organic materials with aromatic rings having high non linear optical coefficient, higher laser damage threshold, fast response, low mobility, and large band gap find many applications [5–8].

Ninhydrin $C_9H_6O_4$(2,2-Dihydroxyindane-1,3-Dione) is one such organic materials with high melting point and two

hydroxyl groups attached to the same carbon atom. It is used to detect ammonia or primary and secondary amines and fingerprints. It is also used in amino acid analysis of proteins. Ninhydrin molecules play a vital role in many fields like soil biology, chemistry, agriculture, medicine, forensic, food science, and so on. Also it is a potential material for micromolar determination of human serum albumin based on chemiluminescence and microbial activity [9]. Recently, Uma Devi et al. found the suitability of ninhydrin crystals for the nonlinear optical applications and found that second harmonic generation efficiency is five times that of KDP. Ninhydrin crystallizes in a noncentrosymmetric space group of $P2_1$and belongs to monoclinic system [10]. Uma Devi et al. already reported the growth and characterization of pure ninhydrin [11] and urea with ninhydrin [12] and stated that urea ninhydrin monohydrate crystal crystallizes in centro symmetric space group of P21/c. The addition of some transition metal ions is expected to influence the growth kinetics, habit modification, and the large-size single crystals. The presence of small amount of impurities such as Ni^{2+}, Cu^{2+}, and Mg^{2+} plays an important role in the growth rate, habit modification of the crystal, and its properties [13]. An impurity can suppress, enhance, or stop the growth of crystal completely. The impurity effect depends on the impurity concentration, super saturation, temperature, and pH of the solution and this can be successfully explained already for many NLO crystals [14]. In the present work, we report the growth of Cu^{2+}-doped ninhydrin single crystals and studied the effect of Cu^{2+} in the system.

2. Materials and Methods

Single crystals of Cu^{2+} doped ninhydrin were grown by slow evaporation method. To the 100 mL saturated solution of ninhydrin, 0.2% of $CuCl_2$ was added slowly and stirred well for nearly 2 hours, then filtered, and allowed to cool. Within 10 days tiny, pale yellow crystals of dimension 5.07 mm × 3.41 mm × 2.69 mm were harvested.

2.1. Characterization. The grown crystals have been subjected to various characterization studies like single crystal XRD, FT-IR, dielectric, and SHG. The grown crystals of the title compound were subjected to single crystal XRD analysis using ENRAF Nonius AD4/MAC4 X-ray diffractometer with M_oK_α (λ = 0.71073 Å) radiation. The grown crystals have also been characterized by X-ray powder diffraction technique using Rich Seifert X-ray powder diffractometer with CuK_α radiation of λ = 1.5406 Å. The 2θ range was analyzed from 10° to 70° by employing the reflection mode for scanning. The detector used was a scintillation counter. The UV-Visible spectrum of the grown crystal was recorded between 200 and 1200 nm using CARY/5E/UV spectrophotometer. A Perkin Elmer Spectrum one FT-IR spectrometer was employed to record the IR spectrum to analyze the functional groups present in the crystals. The sample for this measurement was finely grounded and mixed with KBr. The dielectric study was carried out using the instrument, HIOKI model 3532-50 LCR HITESTER. Samples of known dimension (5.07 mm × 3.41 mm × 2.69 mm) were silver coated on the opposite faces and then placed between the two copper electrodes to form the parallel plate capacitor. The capacitance of the sample was noted for the applied frequency that varies from 100 Hz to 5 MHz at different temperatures (353 K and 373 K). The grown crystals of ninhydrin were subjected to Kurtz second harmonic generation test by using Nd:YAG Q switched laser beam with input pulse of 0.68J for the non linear optical property.

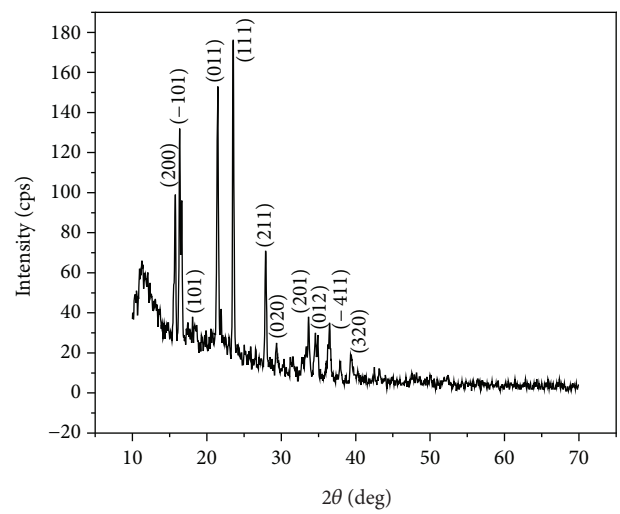

Figure 1: Indexed X-ray powder diffraction pattern Cu^{2+} doped ninhydrin.

3. Results and Discussion

3.1. Single Crystal XRD. The single crystal XRD data of the title crystal indicates that it crystallizes in the monoclinic system with noncentrosymmetric space group $P2_1$ with lattice parameters a = 11.28 Å, b = 5.98 Å, c = 5.71 Å, α = 90°, β = 98.57, γ = 90°, and V = 381 (Å)^3, which agrees very well with the reported value [10]. It is observed that there is a slight change in unit cell parameters which reflects the lattice distortion due to the substitution of Cu^{2+} [15].

3.2. Powder X-Ray Diffraction Analysis. The crystal structure of ninhydrin was reported by Medrud [10]. The title crystal crystallizes in monoclinic with space group $P2_1$. Figure 1 shows the indexed X-ray powder diffraction pattern of the grown title crystal. The results agree well with XRD pattern of ninhydrin molecule [11]. Appearance of sharp and strong peaks confirms the good crystallinity of the grown crystals. The prominent peaks have been indexed. A small change in the intensity level of the peaks and peak position at the higher angle side is due to the addition of copper.

3.3. Optical Transmission Spectral Analysis. The UV-Vis spectrum gives information about the structure of the molecule that the absorption of UV and visible light involves in the promotion of electrons in σ and π orbital from the ground

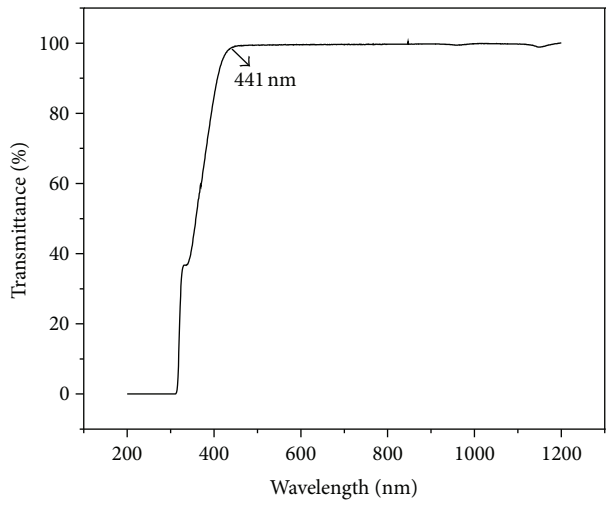

Figure 2: Optical transmission spectrum Cu^{2+} doped ninhydrin.

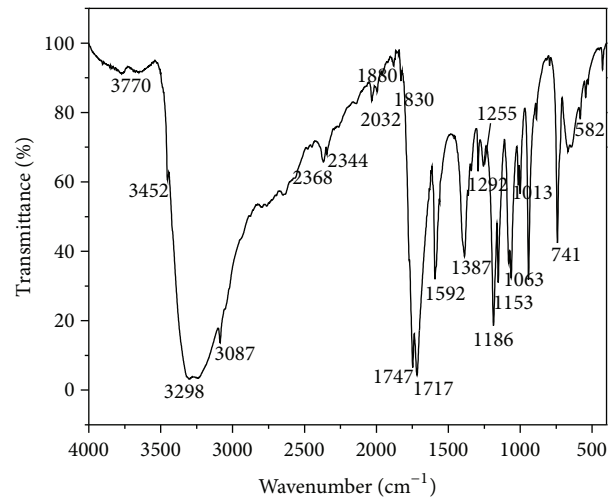

Figure 3: FTIR spectrum of Cu^{2+} doped ninhydrin.

state to higher energy state. The UV transmission spectrum of grown crystal is shown in Figure 2. The determination of UV transparency and cutoff wavelength is very important since these crystals are mainly used in optical application. The lower cut off wavelength is found to be 314 nm and upper cut off wavelength is 441 nm. Between 450 and 1200 nm, there is no absorption of wavelength which clearly indicates that grown crystals can be used as window material in optical instruments. The small peak at 339 nm is due to n-π^* transition [16]. High transmittance % observed from 450 nm indicates that the crystal possesses good optical transparency for SHG of Nd:YAG laser.

3.4. FTIR Analysis. Fourier Infrared spectrum was recorded using KBr pellet technique in the range 400–4000 cm^{-1} and the recorded FTIR spectrum is shown in Figure 3. Vibrational spectroscopy provides an important tool to understand the chemical bonding.

The strong absorption peak at 3298 cm^{-1} is due to O–H symmetric stretching [12] and 3087 cm^{-1} is due to aromatic C–H stretching. The carbonyl (C=O) peak is observed at 1747 cm^{-1} and 1717 cm^{-1}. A medium intense peak observed at 1592 cm^{-1} is attributed to aromatic ring vibration [17]. Peaks at 1292 cm^{-1} and 741 cm^{-1} are attributed to in-plane bending modes of aromatic C–H bonding and out-of-plane aromatic C–H bonding, respectively [18]. The peaks at 1063 cm^{-1}, 1153 cm^{-1}, 1186 cm^{-1}, 1255 cm^{-1}, and 1292 cm^{-1} are attributed to the plane bending modes of aromatic C–H bonds.

3.5. Dielectric Studies. The dielectric properties are associated with the electro-optic property of materials, particularly when they are nonconducting materials [19]. Microelectronics industry needs low ε_r materials as an interlayer dielectric. Figures 4 and 5 show the variations of dielectric constant and dielectric loss of the title crystal at two different temperatures, that is, 353 K and 373 K, as a function of frequency.

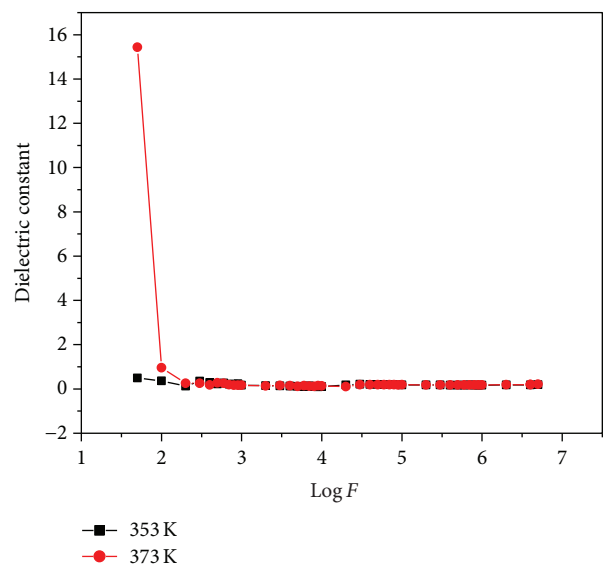

Figure 4: Variation of Dielectric constant with frequency for different temperatures.

The dielectric constant is calculated using the formula

$$\varepsilon' = \frac{Ct}{\varepsilon_o A}, \quad (1)$$

where C is capacitance (farad), t is the thickness (metre), A the area (m^2), ε_o is the absolute permittivity in the free space having a value of 8.854×10^{-12} Fm^{-1}.

It is seen that the value of dielectric constant is found to decrease and attain constant values in the higher frequency region. The decrease in dielectric constant of the title crystal at low frequencies may be attributed to the contribution of the electronic, ionic, orientation, and space charge polarizations which depend on the frequencies. At low frequencies all the four contributions are active [20]. The low value of ε_r at

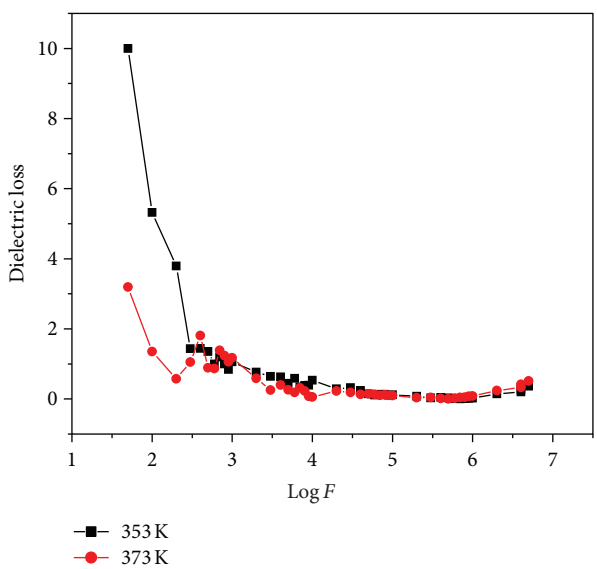

FIGURE 5: Variation of dielectric loss with frequency for different temperatures.

high frequencies are important for these materials in the construction of photonic and NLO devices which suggests that the sample possesses enhanced optical quality with low level defects [20–22]. Dielectric loss decreases with increase in frequency. The larger value of ε_r and tan δ at low frequency arises due to the presence of space charge polarization near the grain boundary interfaces which depends on the purity and perfection of the sample [22].

3.6. SHG Test. Second harmonic generation test was performed to find the NLO property of the grown crystal by using Kurtz-Perry technique [23]. Nd:YAG laser using the first harmonics output of 1064 nm with pulse width of 8 ns and repletion rate 10 Hz was passed through the sample. The green signal was emitted which confirms the second harmonic generation efficiency.

4. Conclusion

Single crystals of Cu^{2+} doped ninhydrin were grown by slow solvent evaporation technique. Single crystal XRD confirmed the unit cell parameters with the reported value. In powder X-ray diffraction pattern, appearance of sharp and strong peaks confirms the good crystallinity of the grown crystals also the prominent of peaks has been indexed. UV-Vis-NIR study reveals the suitability of the crystal for NLO applications and the lower cut off wavelength is found to be 314 nm and upper cut off wavelength is 441 nm. There is no absorption of wavelength in the entire visible region. FT-IR spectrum gives the various functional groups present in the structure. A medium intense peak observed at 1592 cm^{-1} is attributed to aromatic ring vibration. The carbonyl (C=O) peak is observed at 1747 cm^{-1} and 1717 cm^{-1}. The other stretching modes have also been assigned. From the dielectric study, it is found that both dielectric constant and dielectric loss of the crystal decrease with increase in frequency. The emission of green signal confirms the second harmonic generation efficiency of the crystal. Thus, the moderate SHG efficiency and encouraging dielectric properties of the crystal indicate the suitability of this crystal for photonic device fabrication.

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