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GROWTH, SPECTRAL, OPTICAL AND ELECTRICAL PROPERTIES OF 2-AMINOPYRIDINIUM COPPER ACETATE SINGLE CRYSTAL

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Semi-organic 2-aminopyridinium copper acetate (2-APC) single crystal was grown from aqueous solution by slow evaporation method. Single crystal X-ray diffraction studies confirm that 2-APC crystallizes in monoclinic crystal system with centrosymmetric space group $P2_1/c$. Powder X-ray diffraction studies revealed the crystallinity nature of 2-APC crystal. FTIR spectral analysis was used to confirm the presence of functional groups of 2-APC compound. UV-Visible and Photoluminescence optical studies were carried out for the grown 2-APC crystal. The dielectric studies reveal that the grown crystal has low dielectric constant and dielectric loss values at higher frequency region. It indicates that the grown 2-APC crystal possesses good optical quality with lesser defects.

Keywords: Crystal growth; X-ray diffraction; Photoluminescence; Electrical studies;

1. INTRODUCTION

Elucidating the relationship between the compositions, structures and properties of materials, and developing new materials are two of the most important issues in the area of materials science. Hence, there has been continuous demand to develop new materials which are cost effective, easier way of fabrication and to explore its processability in growing technologies [1]. Even though organic materials with aromatic ring have been attracting much attention because of their high nonlinearity, fast response and high optical damage threshold, their practical applications are limited due to poor mechanical, thermal stabilities and the inability to produce and process large crystals. Semi-organic crystals typically have high melting point, excellent mechanical, thermal properties and high degree of chemical inertness but unfortunately they have relatively modest nonlinearities compared with their organic counterparts. In this view semi-organic complexes possessing the advantages of both the organic and inorganic materials have been created great interest among the researchers in the development of many new materials for frequency conversion applications [2-4]. Semi-organic materials include organic and inorganic salts and metal organic coordination complexes have been studied [5-7]. In the present investigation, semi-organic 2-aminopyridinium copper acetate crystal has been successfully grown from aqueous solution by solution growth method and the structural, optical, and electrical properties of grown crystal have been studied.

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2. EXPERIMENTAL

2.1 Material Synthesis, Solubility and Crystal Growth

Commercially available 2-aminopyridine (Loba Chemie-98%) and copper acetate (Merck-99%) in the stoichiometric ratio were dissolved in Millipore water. The solution was stirred for 4 h and after attaining saturation, the solution was filtered and kept in a clean environment. After four days, crystals were obtained by spontaneous nucleation. As the solubility of the material plays a vital role in yielding good shaped crystals, it is desired to select a suitable solvent for the material, where the solute is moderately soluble. The solubility of 2-APC in Millipore water was determined as a function of temperature varying from 30 to 60º C. After attaining saturation, the equilibrium concentration of the solute was analyzed gravimetrically. The corresponding solubility curve was depicted in Fig.2 and showed that the solubility increases significantly with increasing temperature which favours for bulk growth of crystals.

The prepared solution was continuously stirred for 5 hr at constant temperature using a temperature controlled magnetic stirrer to have homogeneously mixed solution. Then, the solution yielded the precipitate of crystalline substance of 2-APC. The synthesized material was purified by successive recrystallization process. The saturated solution was prepared at 35°C according to the solubility data. Then, the prepared solution was filtered and covered with a perforated polythene sheet to restrict the fast evaporation of the solvent. The prepared growth solution was kept in a constant temperature bath with control accuracy ±0.01 °C. By adopting solvent evaporation technique, 2-aminopyridinium copper acetate single crystal with dimension 7 x 6 x 4 mm^3 was grown and grown crystal was harvested after a span of 3-4 weeks. The photograph of as-grown 2-APC crystal is shown in Fig.1.

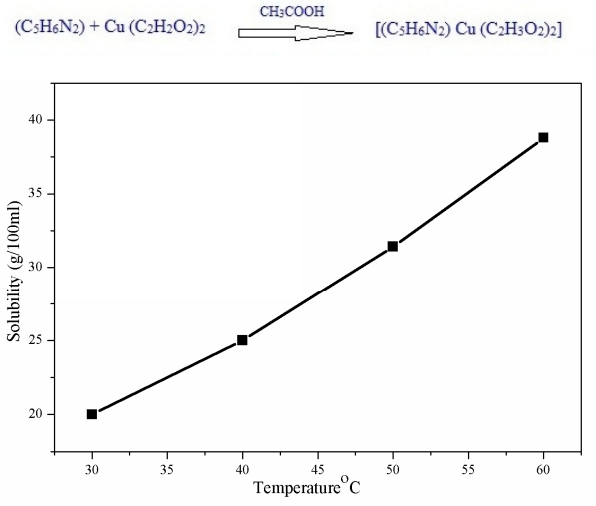


FIGURE.1 Solubility of 2-APC in water

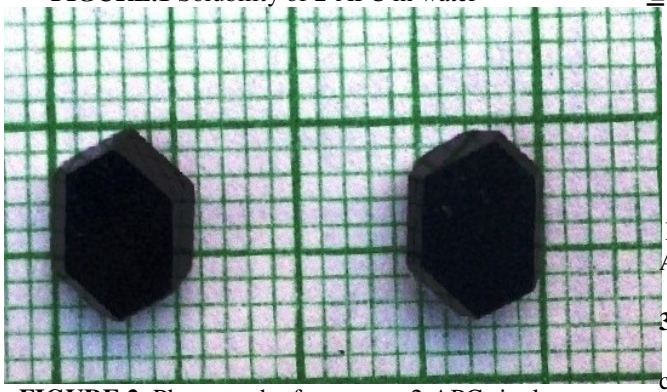


FIGURE.2: Photograph of as-grown 2-APC single crystals

3. Results and Discussion

3.1 X-ray diffraction study

Single crystal X-ray diffraction study was performed by using Bruker Nonius CAD-4/MACH3 single crystal X-ray diffractometer. Lattice parameters value was found to be a = 7.523 Å, b = 19.74 Å, c = 8.23 Å, β = 114.32°, V = 1083.82 $Å^3$ and the grown crystal belongs to monoclinic system with centrosymmetric space group $P2_1/c$ and it is close agreement with reported data [8]. Powder X-ray diffraction analysis was performed by using Bruker AXSCAD4 diffractometer with CuK_α (λ = 1.5405 Å) radiation to study the crystalline quality. The crystal was then grounded finely and subjected to powder X-ray diffraction study. The PANalytical X'Pert Powder XRD system was used to record reflections from various planes and the hkl values were determined using the HighScore plus program. The recorded powder X-ray diffraction pattern of the grown crystalline sample is shown in Fig.3. The full width half maximum of sharp intensity peaks at 2θ=13 degree with hkl values (0 1 1) was found to be 0.21 degree which indicates the good crystallinity of the grown 2-aminopyridinium copper acetate crystal. The well-defined Bragg's peaks at specific 2θ values for crystal planes and its corresponding Miller indices were indexed.

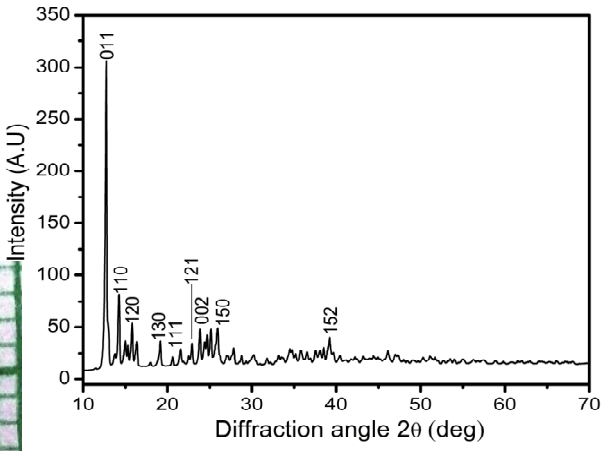


FIGURE.3 Powder X-ray diffraction pattern of 2-APC crystalline sample

3.2 FTIR Spectral Analysis

FT-IR spectrum of 2-aminopyridinium copper acetate recorded in the range 4000-400 cm^{-1} by KBr pellet technique in nitrogen atmosphere is shown in Fig.4. The peak appeared

close to 3420 cm^{-1} is assigned to OH group. Hence, the pyridine nitrogen might be protonated in the crystal. The intense peak appeared at 2927.38 cm^{-1} is due to C-H stretching vibration. The C=O carbonyl stretching vibration occurred at 1669 cm^{-1}. The C=C stretching vibration appeared at 1628 cm^{-1}. The peak yielded at 1523.25 cm^{-1} is due to C-C stretching vibrations. The C-N stretching vibration yielded a peak at 1350.17 cm^{-1}. The peaks appeared at 1243.13, 1201.33 and 1124.20 cm^{-1} are due to C-O stretching vibrations. The bending modes of C-H occurred at 994.72, 945.53 and 780.67 cm^{-1}. Hence, the FTIR spectrum confirmed the formation of 2-aminopyridinium copper acetate crystal and vibrational frequency assignments are listed in Table 1.

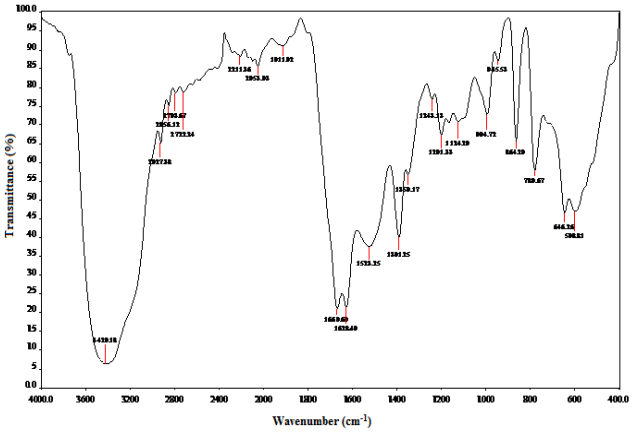


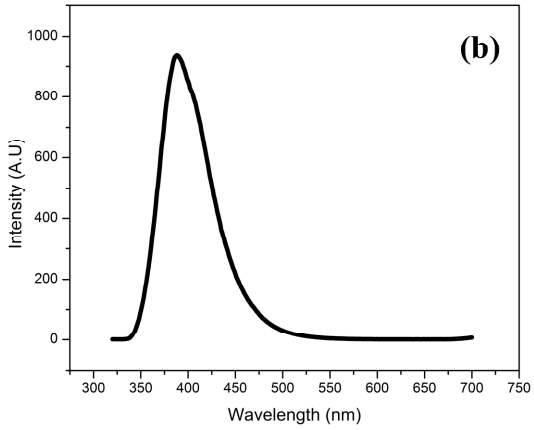
FIGURE 4 FT-IR spectrum of 2-APC crystalline sample

Table 1 FTIR vibrational frequencies assignments of 2-APC crystalline sample

Assignments	Wavenumber (cm^{-1})
OH stretching vibration	3420.18
C-H stretching vibration	2927.38
C=O carbonyl stretching	1669
C=C stretching vibration	1628
C-C aromatic stretching	1523
C-N stretching vibration	1350.17
C-O stretching vibration	1243013
C-H in-plane bending	994.72

3.3 Optical study

UV-Vis transmission spectral analysis of 2-APC crystal was carried out between 190 nm and 900 nm using PerkinElmer Lamda 35 UV-VIS-NIR Spectrometer, covering the entire visible and near infrared region. The grown crystal was cut and polished to thickness of about 2 mm and crystal free from any noticeable defects was taken for UV–Visible transmission study. From the Fig.5a, it was observed that 2-APC crystal has UV cut-off wavelength around 332.51 nm and the transmission percentage was found to be 44 %. Transmission in the near ultraviolet region arises from electronic transitions associated within the samples. Photoluminescence (PL) technique, the spectrum emitted by the radioactive recombination of photo-generated minority carriers, is a direct way to measure the band



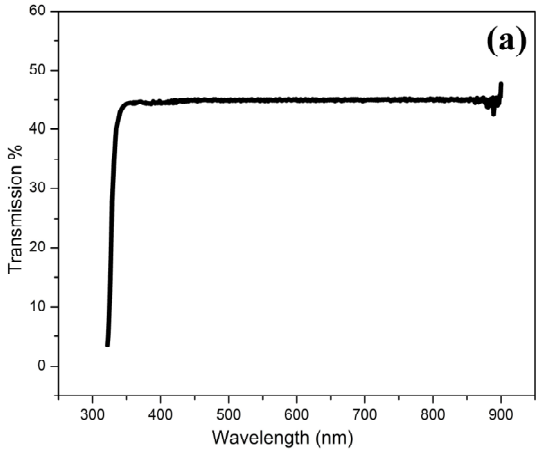


FIGURE.5 (a) UV-Visible transmittance spectrum and (b) Photoluminescence spectrum of 2-APC crystal

gap energy. The excitation and emission spectra of 2-APC were recorded by using RF-5301 spectrofluorometer. The excitation spectrum was traced in the range 320-700 nm. The sample was excited at 310 nm, a peak observed at 387.9 nm in the emission spectrum is shown in Fig.5b. The band gap energy was found to be 3.19 eV.

3.4 Dielectric study

Dielectric response in crystals reveals information about the electric field distribution and charge transport mechanism. Dielectric studies of the grown crystal were carried out in the frequency range 100 Hz – 6 MHz with temperatures varying from 40-70°C. The dielectric constant ε_r and dielectric loss (tan δ) were calculated using the relations,

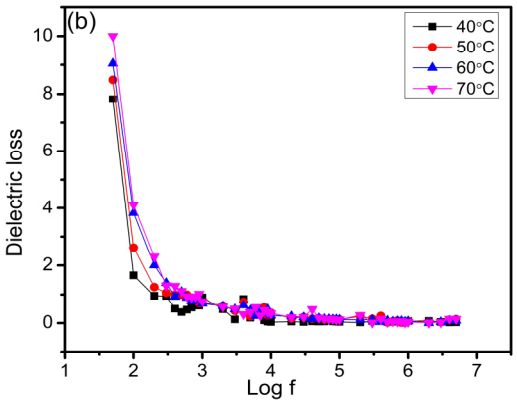
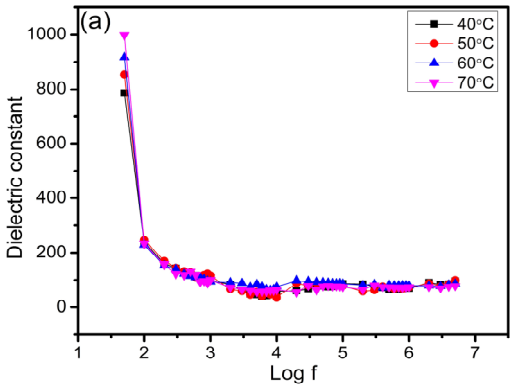


FIGURE. 5(a) Plot of dielectric constant vs. Log f and (b) Plot of dielectric loss vs. Log f of 2-APC crystalline material

$$\varepsilon_r = C\ t\ /\varepsilon_0\ A \quad (1)$$

$$\tan\delta = \varepsilon_r\ D \quad (2)$$

where C is the capacitance, t is the thickness of the crystal, ε_0 is the permittivity, D is the dissipation factor and A is the area of cross-section.



The plots of dielectric constant and dielectric loss versus frequency were drawn as shown in Figure 5(a&b). The dielectric constant as a function of both frequency and temperature was measured and it was observed that dielectric constant decreases with increase in frequency, which is usually referred as anomalous dielectric dispersion. The larger value of dielectric constant at low frequency enumerates that there is a contribution from all four known sources of polarizations namely electronic, ionic, dipolar and space charge distribution. The space charge polarization is generally active at lower frequencies. The variation of ε_r and tanδ with frequency may be considered as the normal dielectric behavior of title material.

4. Conclusion

Single crystal of 2-APC was grown by slow evaporation technique and its solubility in water solvent was estimated. X-ray diffraction study of 2-aminopyridinium copper acetate crystal confirmed the monoclinic structure and good crystallinity nature. Linear optical studies reveal that the 2-APC crystal show good transmission in the entire visible region with lower cut-off wavelength 332.51 nm. Optical behavior 2-APC crystal was examined by photoluminescence excitation spectral analysis. The dielectric study reveals that 2-APC crystal exhibits normal dielectric behavior.

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