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RESEARCH ARTICLE

SYNTHESIS, GROWTH AND CHARACTERIZATION OF THE METAL COORDINATED COMPLEX: 2-AMINOPYRIDINE COPPER ACETATE SINGLE CRYSTAL.

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Abstract

The metal coordinated complex of 2-aminopyridinium copper acetate (2APC) crystals was grown by slow evaporation solution growth method from the solvent ultrapure water. The Single crystal X-ray diffraction studies for 2APC crystal confirm the grown crystal belongs to the monoclinic crystal with the space group of P21/c in centrosymmetric system. Powder X-ray diffraction studies reveal2 the crystal perfection of as grown 2APC crystals. FTIR analysis was performed to confirm the presence of functional groups in 2APC crystal. The optical UV-Visible studies were carried out for the grown 2APC crystal. Thermal behavior of the 2APC crystal has been investigated by TG-DTA analyses. The dielectric study shows the grown crystal has low dielectric constant and dielectric loss values at high frequency region. The NMR studies shown that shifts are due to metal–ligand coordination complex. The magnetization values for 2APC crystal are the Saturation magnetization (Ms) is 0.229 x 10^{-3} emu/g, the retentivity (Mr) is 4.595x10^{-6} emu/g and coercivity (Hc) is 444.95 G. The material referred to as soft magnetic materials.

Introduction:-

The being of ferromagnetic and ferroelectric orders in single crystal materials requires the advanced materials design. Ferro electricity, which associated with atoms in most materials that have empty d-orbits, where as magnetism requires for the ferroelectric materials partially with filled d-orbits. There has been great interest in multi ferroics in the field of research and developments in ferrous materials based properties (Eerenstein W, Mathur N. D, 2006, Cheong, S.W, Mostovoy M, 2007). Ferroelectricity can be implemented in the alternative ways, such as magnetic cycloidal order (Kimura T, 2007), charge ordering (Van den Brink J. Khomskii D, 2008) and spin-Peierls distortion for scientific studies (Kagawa F, Horiuchi S, Tokunaga M, Fujioka J, Tokura, Y, 2010). Ferromagnetism is important for potential applications, they have the strength of the coupling between the order parameters and they are the direct control of the magnetization by an electric field and vice versa (Tokura, Y, Seki S, 2010, Wu S. M, Cybart S. A, Yu P, Rossell M. D, Zhang J. X, Ramesh R, Dynes R. C, 2010, Ohkoshi S, Tokoro H, Matsuda T, Takahashi H, Irie, H., Hashimoto K. Angew, 2007). Due to the multi ferroic order the Perovskite based organic and inorganic hybrid compounds show the outstanding candidatures for their combine structural flexibility with robust

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magnetic and electrical properties (Mitzi, D. B., 1999). The hydrogen-bond network of ferroelectrics is equal to the halogen atoms. Ammonia end group of the organic component (Horiuchi S., Tokura Y, 2008) such as ammonium Rochelle salt (Ishibashi Y. Takagi Y, 1976) and triglycine sulfate (TGS) (Hoshino, S, Okaya, Y. Pepinsky R, 1959) play the potential roles. Since, the potential of hybrid organic and inorganic compounds has been emphasized by Jain et al as they are a new route toward multi ferroics (Jain, P, Ramachandran, V, Clark, R. J, Zhou, H. D, Toby, B. H, Dalal, N. S, Kroto, H. W, Cheetham, A. K, 2009).

Experiment:-

Material synthesis and Crystal growth:-

Commercially available 2-aminopyridine and copper acetate were dissolved in ultrapure water with Millipore of 18.2 MΩ. Cm in the stoichiometric ratio of 1:1under room temperature. The continuous stirring for 5 hours at a constant temperature at 30°C using a magnetic stirrer which results in the formation of crystalline substance of 2-aminopyridinium copper acetate 2APC. The material was purified by a successive recrystallization process. The 2APC single crystals were grown in aqueous solution by slow evaporation technique. The saturated solution was prepared at 38°C according to the solubility data. The prepared homogenous solution was further filtered and covered with a polythene sheet to avoid the dust particle deposition and to restrict the fast evaporation of the solvent. Then the prepared solution was kept in a constant temperature bath with control accuracy of ±0. 01°C. After a period of weeks, an optimum size single crystal with dimension of 6 x 7 x 4 mm^3 was harvested and the photographs of the as grown and cut and polished 2AC crystal are shown in Fig.1.

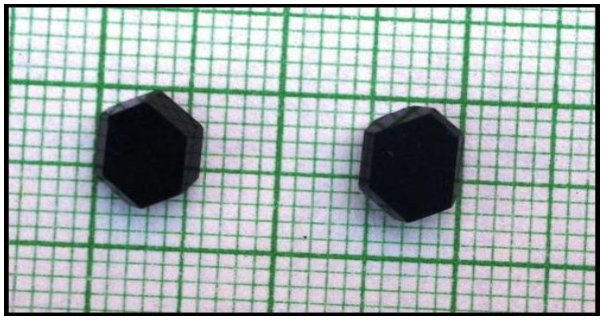


Fig.1:- Photograph of as-grown 2APC single crystal

Results and discussion:-

Single crystal X-ray diffraction analysis:-

Single crystal X-ray diffraction study of grown crystal was performed by using Bruker Nonius CAD-4/MACH 3 single crystal X-ray diffractometer. The grown crystal belongs to centrosymmetric space group P21/c with monoclinic system and is close agreement with reported data (Sieron,L, 2004). The estimated cell parameter values of 2APC crystal are listed in Table 1.

Powder X-ray diffraction:-

Powder X-ray diffraction analysis was performed to study the crystalline quality of the 2APC crystal by using Bruker AXSCAD4 diffractometer with CuKα radiator with wavelength of 1.5405 Å. The recorded powder X-ray diffraction pattern of the grown crystal is shown in Fig. 2. The sharp intensity peaks of grown 2APC crystals from the plot indicate the good crystalline nature.

Table 1:- Single crystal data of 2-aminopyridinium copper acetate (2APC) crystal.

Crystal data	**2-aminopyridinium copper acetate**
a (Å)	7.523
b (Å)	19.742
c (Å)	8.235
α = γ	90^o
β	114.32^o
V	1083.82
Crystal system	Monoclinic
Space group	P21/c

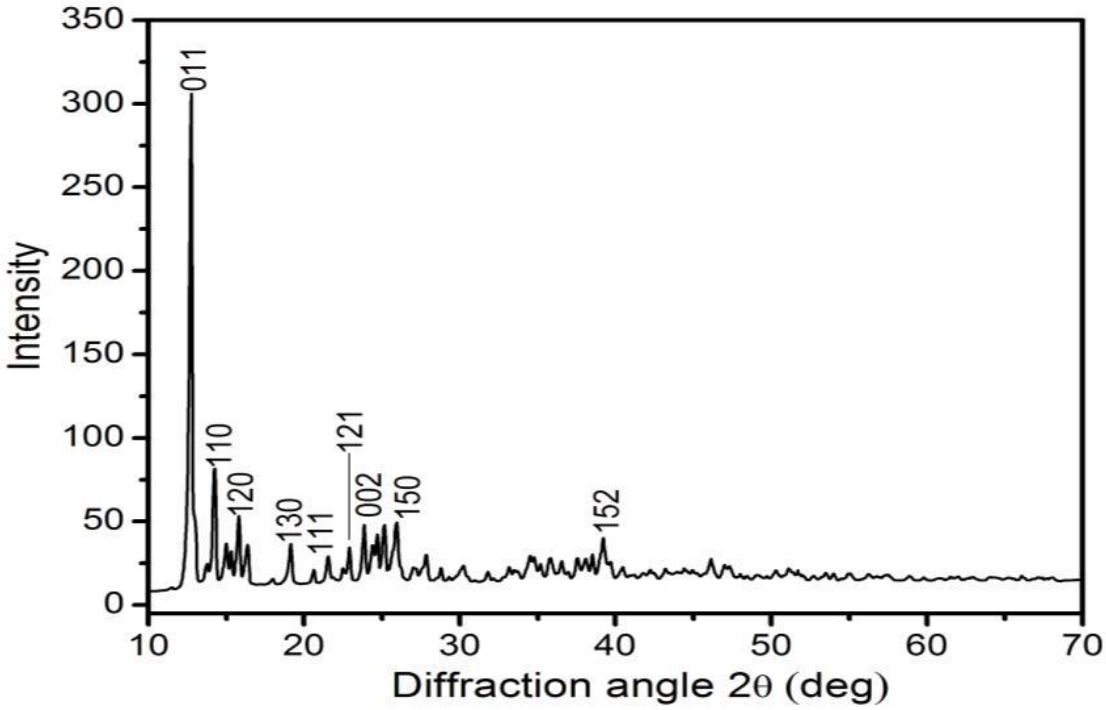


Fig.2:- Powder X-ray diffraction pattern of 2APC crystal

FT-IR Studies:-

By KBr pellet technique in a nitrogen atmosphere, the FT-IR spectrum of 2-aminopyridinium copper acetate recorded in the range 4000-400 cm^{-1} and the peak close to 3420 cm^{-1} is assigned to N-H stretching primary amines. Hence the pyridine nitrogen might be patented in the crystal. The intense peak at 2927.38 cm^{-1} is due to C-H stretching vibration. A peak occurs at 1669 cm^{-1} assigned to the C=O carbonyl stretching vibration. The peak at 1628 cm^{-1} and 1523.25 cm^{-1} are due to C=C and C-C stretching vibrations. The C-N stretching vibration yielded at a peak of value 1350.17 cm^{-1}. The intense peaks at 1243.13, 1201.33 and 1124.20 cm^{-1} regions are assigned to the C-O stretching vibrations. The peak at 994.72, 945.53 and 780.67 cm^{-1} shows the bending modes of C-H stretching. Hence, the IR spectrum confirmed the presence of 2-aminopyridinium copper acetate crystal as shown in Fig.3 and is listed in Table.2.

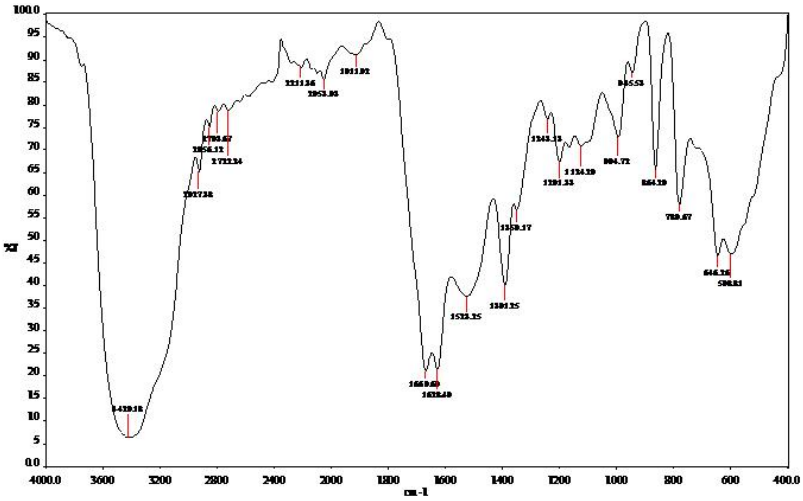


Fig 3:- FT-IR spectrum of 2APC crystal

Table 2:- Assignment of FTIR vibrational frequencies of 2APC crystals

Assignments	Wavenumber (cm^{-1})
N-H stretching primary amines	3420
C-H stretching	2927.38
C=O carbonyl stretching	1669
C=C stretching vibrations	1628
C-C aromatic stretching	1523
C-N stretching vibrations	1350.17
C-O stretching vibrations	1243.13
C-H in plane bending	994.72

UV-Vis Spectral Studies:-

Using PerkinElmer Lamda 35 UV-VIS-NIR Spectrometer, the UV-Vis absorptions spectral analysis of 2APC crystal was carried out by covering the entire visible and near infrared region between 190 nm and 1000 nm. A strong absorption is observed at 332.51 nm which corresponds to the fundamental absorption and UV cutoff wavelength. The 2APC crystal shows good transmission in the entire visible region. Absorption in the near ultraviolet region arises from electronic transitions associated within the samples. Fig.4 shows the UV-Absorption spectrum of the 2APC crystal.

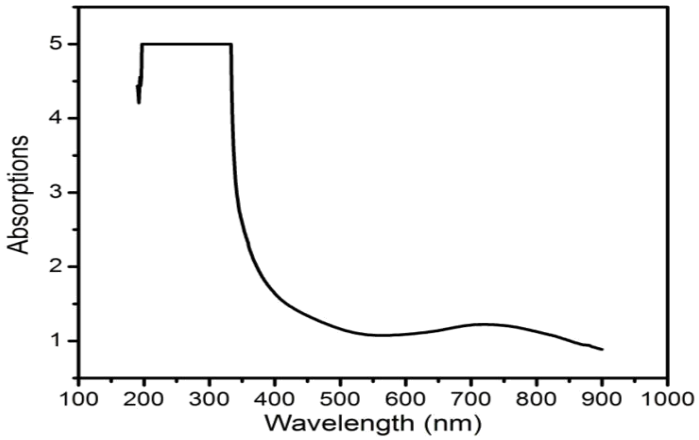


Fig.4. UV-Visible absorptions spectrum of 2APC single crystal

Photoluminescence:-

RF-5301 spectrofluorometer Photoluminescence (PL) instruments used to study the emitted spectrum of photo generated minority carried out by the radioactive recombination process. The excitation and emission spectra of 2APC were recorded in the ranges of 320-700 nm to find the band gap energy. In this shown band, the large amount of impurities induces a large free carrier density. Thus, a large difference carrier interaction causes some of the remarkable modification in the line shape and also the spectral energy of the PL feature (Deshpande, N.G, Sagade, A.A , Gudage, Y.G, Lokhande, C.D, Sharma, R J, 2007). The sample was excited at 310 nm and a peak at 387.9 nm was observed in the emission spectrum is shown in Fig.5. The calculated band gap energy was about 3.19 eV.

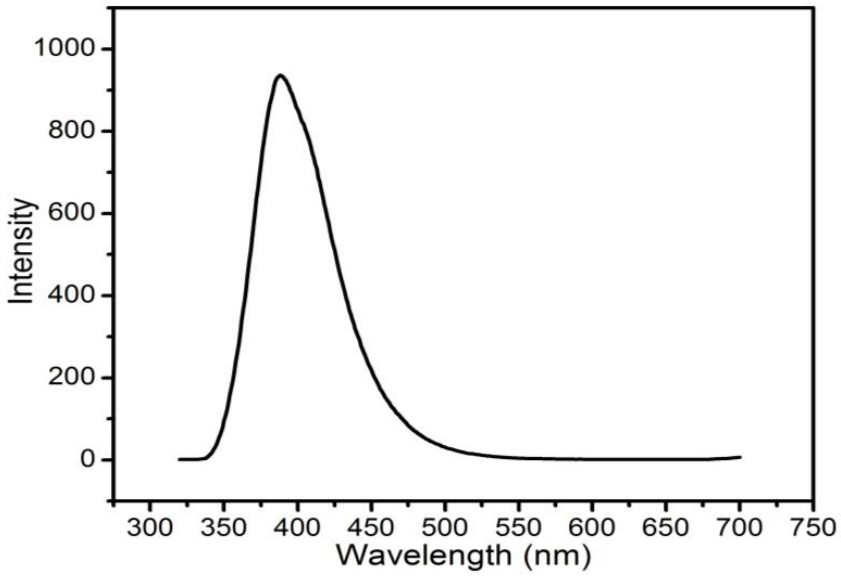


Fig.5:- Photoluminescence spectrum of 2APC crystal

Dielectric studies:-

The dielectric studies were carried out for 2APC crystal in the frequency range 100 Hz to 6 MHz at room for different temperatures. The dielectric constant r was calculated using the relation,

$$r = Ct / \ 0 A, \qquad (1)$$

$$\tan = r D \qquad (2)$$

Where, C and t are the capacitance and the thickness of the 2APC crystal, 0 is the permittivity, D is the dissipation factor and A is the area of cross section. The dielectric constant and dielectric loss versus frequency was plotted as shown in Fig. 6 and Fig.7. The dielectric constant decreases with increase in frequency, which is usually referred to as atypical dielectric dispersion (Pillai, S.O, 2001). The value of dielectric constant is larger at low frequency which enumerates that there is a contribution from for all four polarizations namely electronic polarizations, ionic polarization, dipolar polarization and space charge polarization. Space charge polarization is active at high temperatures with lower frequency values. The changes in dielectric constant and dielectric loss for 2APC may be considered as a normal behavior of dielectric in terms of frequency. The low values of dielectric loss are of reasonably good quality of the grown crystals of 2APC.

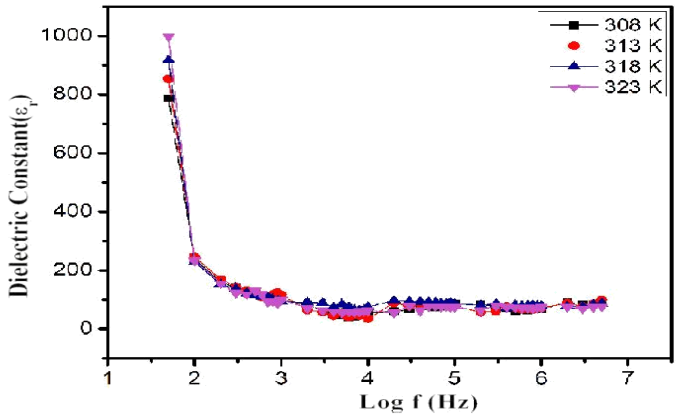


Fig.6:- Plot of dielectric constant vs. Log f of 2APC crystal

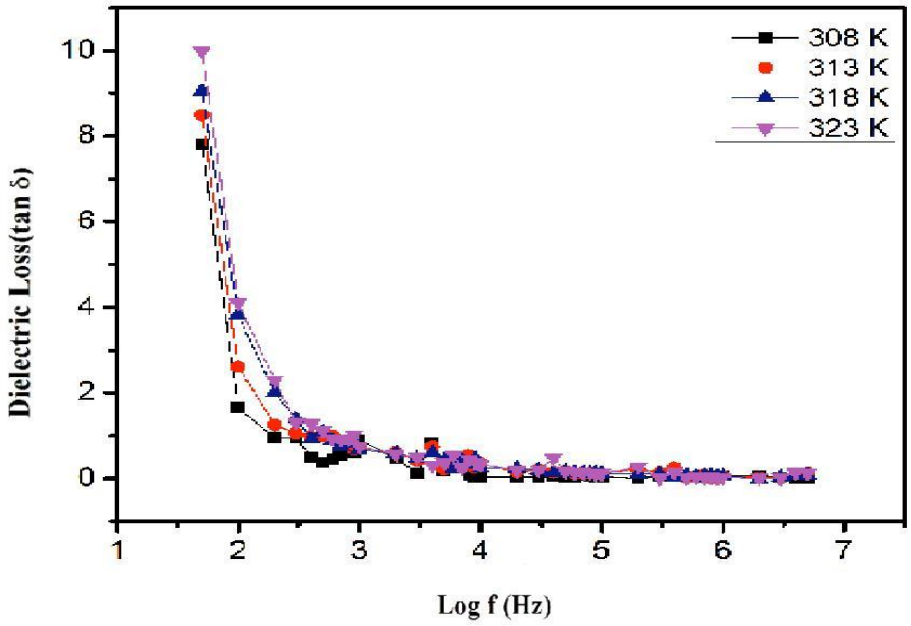


Fig.7:- Plot of dielectric loss vs. Log f of 2APC crystal

Photoconductivity studies:-

The variations of both photo current (Iph) and dark current (Id) with applied field are shown in Fig.8. If photo current is greater than dark current for a given sample the phenomenon is regarded as positive photoconductivity, and the vice versa represents negative photoconductivity. It is seen from the plot, that both photo and dark current of the 2APC increase linearly with the applied electric field. In the present study, it is observed that the photocurrent is higher that the dark current, hence it can be concluded that 2APC exhibits positive photoconductivity. This phenomenon can be attributed to generation of mobile charge carriers caused by the absorption of Photons (Joshi, V.N, 1990).

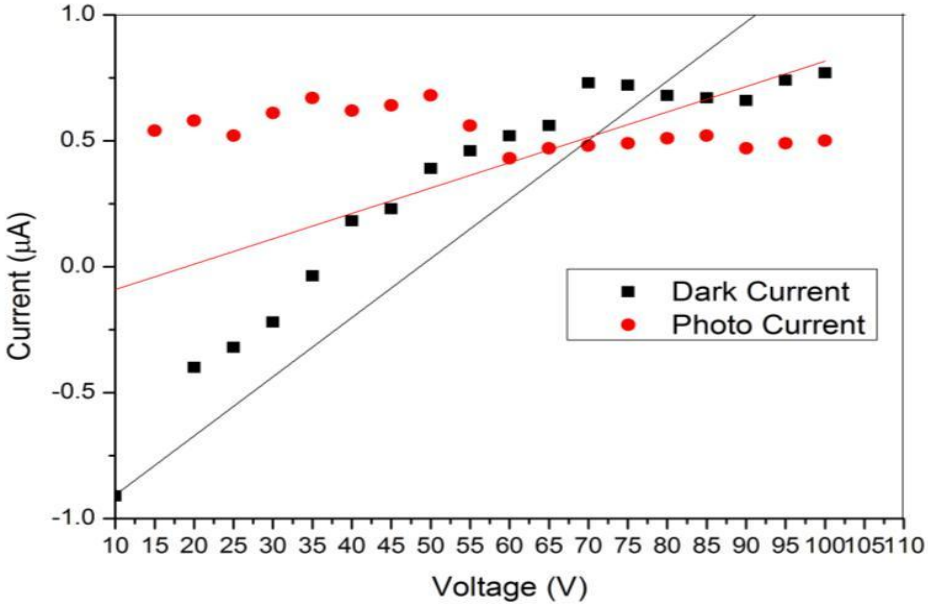


Fig.8:- Photoconductivity spectrum of 2APC crystal

Thermal Analysis:-

Thermal stability of the grown crystal was carried out using NETZSCH STA 449F3 thermal analyzer between room temperature and 800 ºC at a heating rate of 20ºC per minute in the atmosphere of nitrogen gas. In TG curve, it is

observed that there is no major weight loss are absorbed below 184 ºC, decomposition of the material starts from above 184.4 ºC and the second stage decomposition occurs between 210ºC, it may be due to elimination of carbon dioxide molecules. There is no considerable change of weight loss of the material noticed above 600º C. In DTA, there is no endothermic and exothermic trace before 184ºC which reveals that there is no water molecule in this compound, An endothermic is observed at 210ºC may due to the melting point of the compound crystal and ascertain the suitability in NLO applications. The exothermic is observed at about 542ºC may due to the melting point of the oxidization compound crystal good degree of crystallinity of the sample is revealed from the sharpness of the endothermic peak. The Fig. 9 shows the TG/DTA plot of 2APC crystal.

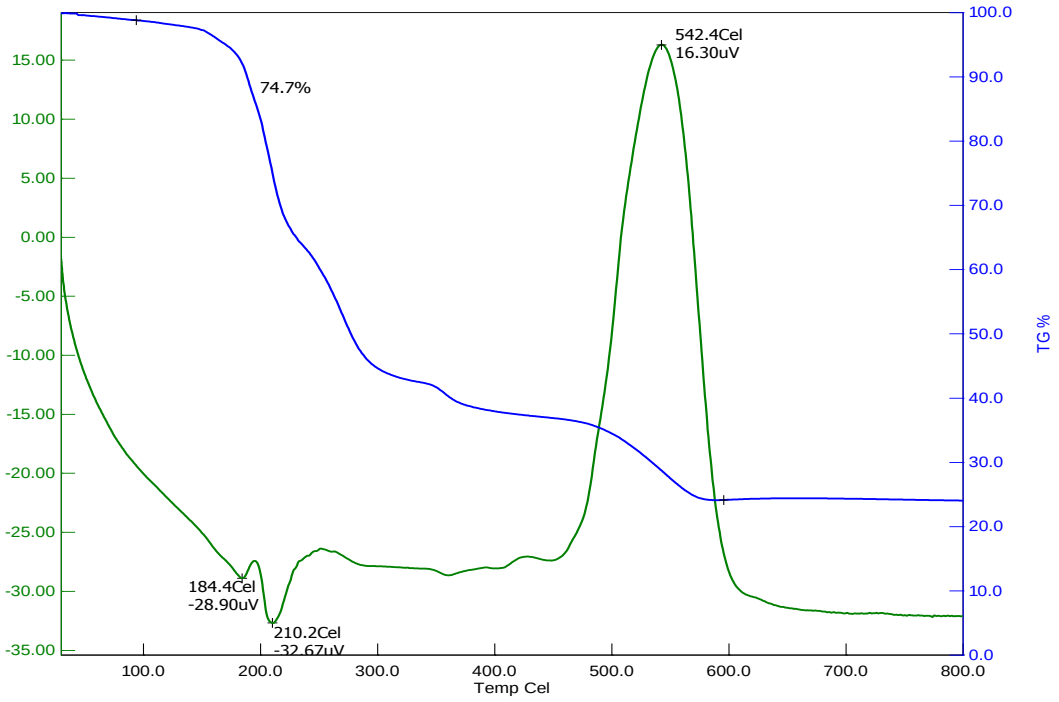
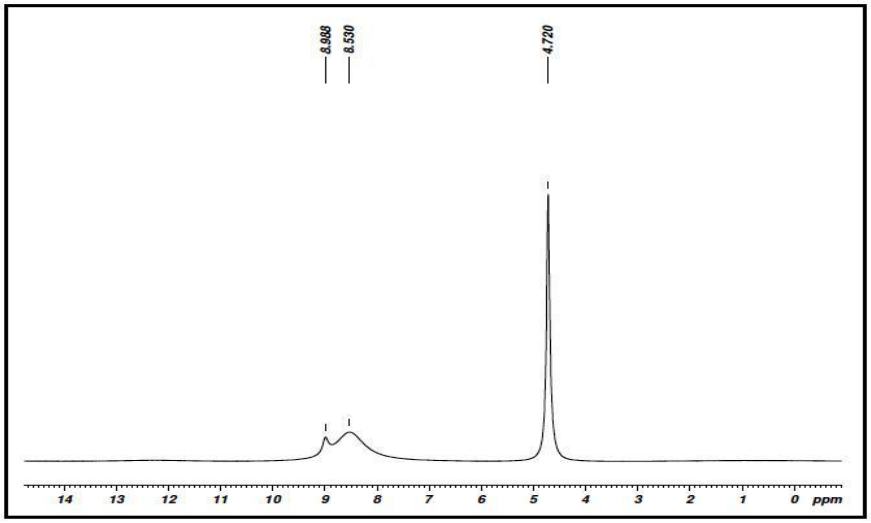


Fig.9:- Plot of TG/DTA of 2APC crystal

FT-^{1}HNMR Analysis:-

The grown 2APC crystal was characterized by ^{1}HNMR spectrometer by using Bruker – AVANCE- III model in the frequency range of 500 MHz with TMS as the internal reference standard. From the show Fig.10, a sharp singlet at δ 4.7 ppm occurs in the downfield for the copper acetate corresponding 2-amino pyridine moiety of NH2 protons. Also, there are the small broadened shifts at around δ 8.5 ppm and δ 8.9 ppm, which indicates that the proton shift are due to metal– ligand coordination in the material complex (Allyn.T, 2010).



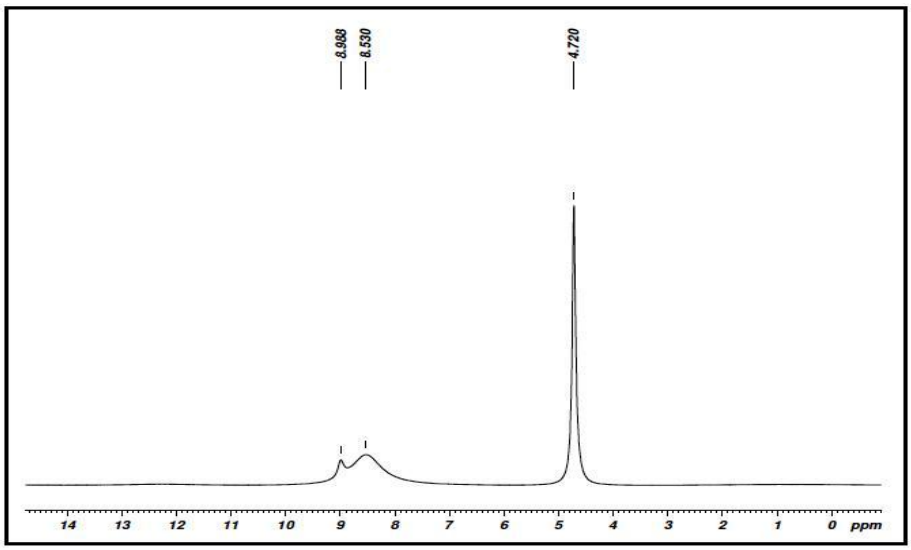


Fig.10:- FT-^{1}HNMR spectrum of 2APC

agnetic studies:-

Magnetic studies were measured for 2APC crystal using the Vibrating Sample Magnetometer (VSM) equipment at room temperature with the constant time of 10 Sec for taking mass of 0.032 g. The plot is obtained between the hysteresis loops of magnetization to the magnetic field strength. From the shown Fig.11, it is stated that, when the magnetic field increases, then the magnetisation value also increases with the presence of metal–organic complexes in the 2APC crystal, which characterize the ferromagnetic hysteresis property of 2APC complex. The obtained hysteresis curve resembles the 'S' shaped curved path which passing through the origin, it confirms the anisotropy crystalline nature. The obtained magnetization values for 2APC crystal are the Saturation magnetization (Ms) is 0.229 x 10^{-3} emu/g, the retentivity (Mr) is 4.595x10^{-6} emu/g and coercivity (Hc) is 444.95 G. Thus, the metal–organic complexes possess soft magnetic interactions, which hold good agreement with reported results (Swapan Das, K, Manas Bhunia, K, Motin Seikh, Md, Saurav Dutta, Asim Bhaumik, 2011) and show that the material referred to as soft magnetic materials because it has a low coercivity value close to the origin.

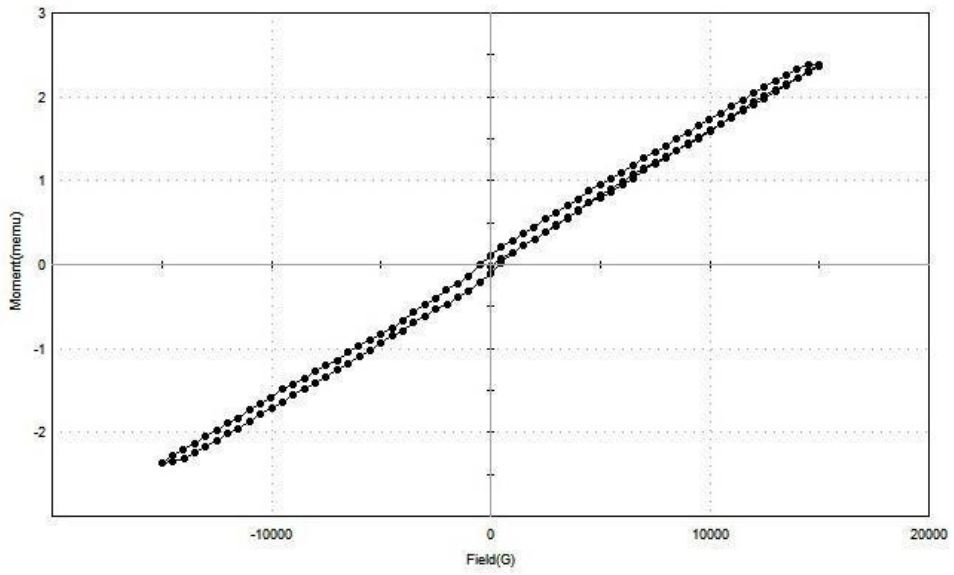


Fig. 11:- Hysteresis loop of 2APC.

Conclusion:-

The 2-aminopyridinium copper acetate (2APC) material was synthesized from aqueous solution and bulk crystal of 2APC has been grown by the slow evaporation method. Single crystal X-ray and powder X-ray diffraction studies confirmed the monoclinic structure of the grown 2APC crystal. The presence of functional groups in the grown

crystal was confirmed from FTIR analysis. From the linear optical studies the 2-aminopyridinium copper acetate crystal show the good transmission in the entire visible region with lower cutoff wavelength 332.51 nm. Its optically high transparency behavior of 2APC crystal was examined by photoluminescence excitation spectral analysis. The dielectric studies revealed that crystal exhibits normal dielectric behavior. It is observed that the photocurrent is higher that the dark current, hence it can be concluded that 2APC exhibits positive photoconductivity. TG curve, it is observed that there is no major weight loss are absorbed below 184 ºC, the decomposition of the material starts from above 184.4 ºC and then the second stage decomposition occurs between 210ºC, it may be due to elimination of carbon dioxide molecules. There is no considerable change of weight loss of the material noticed above 600º C. In DTA, there is no endothermic and exothermic trace before 184ºC which reveals that there is no water molecule in this compound. From NMR, a sharp singlet at δ 4.7 ppm in the downfield correspond to copper acetate related 2-amino pyridine moiety of NH2 protons and a small broadened shifts at around δ 8.5 ppm and δ 8.9 ppm, which indicates that the proton shift are due to metal–ligand coordination in the material complex. This material referred to be as soft magnetic materials because it has a low coercivity value of 444.95 G, which is close to the origin.

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