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GROWTH AND CHARACTERIZATION OF COBALT AND SULPHAMIC ACID DOPED AMMONIUM DIHYDROGEN ORTHOPHOSPHATE: A POTENTIAL NONLINEAR OPTICAL MATERIAL

K.Kumar[1], K. Selvaraju[1], P. Baskaran[2,*] and N. Senthilvelan[3]
[1]P.G. and Research Department of Physics, Government Arts College, Ariyalur-621113, India.
[2]Department of Physics, Government Arts and Science College, Veppanthattai-621116, India.
[3]Department of Physics, Arignar Anna Government Arts and Science College, Attur-636121, India.
*E-mail: pbaskaranphy@yahoo.com

ABSTRACT
The nonlinear optical single crystal of Cobalt (II) sulfate heptahydrate and sulphamic acid doped ADP has been grown by slow evaporation solution growth technique. The powder X-Ray diffraction studies confirmed the grown crystal. The functional group present in the grown crystal was analyzed by FT-IR studies. The thermal and optical behaviors of the grown crystal were studied as function of frequency. SEM analysis was employed to study the surface morphology of the grown crystal. The NLO property of the crystal was tested by Nd:YAG laser.
Keywords: Solution Growth Technique, X-Ray Diffraction, NLO Material, FT-IR.

INTRODUCTION

In recent years, there is growing interest in the study of new nonlinear optical (NLO) materials due to their potential applications in the areas such as optical modulation, optical switching, optical logic gates, frequency shifting and optical data storage in telecommunications, and signal processing.[1-3] Extensive studies on the low order nonlinearities of organic and inorganic materials have been motivated by their wide range of potential applications like second harmonic generation (SHG), electro optic modulation, sum and difference frequency generation, etc. Such materials have large nonlinear optical coefficients, suitable transparency and excellent comprehensive properties.[4,5] Moreover, its lower cutoff wavelength with wide optical transparency window in the visible region makes this material suitable for extensive investigations in photonic device fabrication. [6,7]The crystal with delocalized π –electrons usually possess large NLO response, and it makes attractive for wide range of applications in integrated optics.

Ammonium dihydrogen phosphate (ADP) is an important inorganic crystal and attracts much interest because of their unique piezo-electric, antiferroeletric, electro-optic, dielectric and nonlinear optical properties. ADP matrixes readily accept both organic and inorganic dopants as a representative of hydrogen-bonded material. In the past few decades, a good deal of research work has been done on the growth and characterization of pure and doped ADP crystals.[8-12] A series of dopants like ammonium malate[13], thiourea[14], L-lysine monohydrochloride dihydrate[15], L-alanine[16], L-arginine[17], ammonium acetate[18] and inorganic bimetallic impurities (Ni^{3+}, Mg^{2+})[19] and their influence on various properties of ADP crystals were studied and reported that the addition of impurities in ADP crystal has turned various interesting properties and applications. Sulphamic acid (SA) is the monoamide of sulphuric acid and is highly stable for long period with orthorhombic crystal. It is strong and an important industrial inorganic acid, while mixing it with water and exhibits zwitterionic form.[20] An added advantage in

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sulphamic acid is that large single crystals can be grown from low-temperature solutions.[21] Cobalt sulfate is used in the electroplating and electrochemical industries; as a drier for lithographic inks, varnishes, paints, and linoleum, in storage batteries; and as a coloring agent in ceramics, enamels, glazes, and porcelain. Cobalt (II) sulfate heptahydrate added sulphamic acid crystal have been grown and reported for the first time.[22] In the present investigation, cobalt (II) sulfate heptahydrate, sulphamic acid, and ammonium dihydrogen orthophosphate (CSADP) crystal has been grown successfully by slow evaporation technique and characterized.

EXPERIMENITAL

Growth Procedure

The starting material was synthesized from commercially available Cobalt (II) sulphate heptahydrate, sulphamic acid and ammonium dihydrogen orthophosphate taken in the molar ratio of 1:1:1. The calculated amount of the reactants were thoroughly dissolved in double distilled water and stirred well for two hours to yield a homogeneous mixture. The CSADP single crystals have been grown from aqueous solution by low-temperature solution growth technique by slow evaporation in a constant temperature bath controlled to an accuracy of $\pm 0.01^0$C.CSADP was further purified by repeated recrystallization process for three times using water as a solvent. The recrystallized salt of CSADP was dissolved in water at saturation temperature 32^0C with an optimized solution pH value of 3.5. A saturated solution of 100 ml was taken and the solution was filtered using a filter paper. The filtered solution was taken in a beaker, which was tightly closed with thick filter paper so that the rate of evaporation could be controlled. CSADP transparent single crystals were obtained from the mother solution after fifteen days and shows the as grown crystal of CSADP was shown in Fig.-1.

Fig.-1: Grown CSADP Crystal

Solubility Measurement

The bulk crystals can be grown from slow evaporation technique by selecting suitable solvent and size of the growing crystal depends on the amount of material available in the solution. Hence, the solubility of CSADP in water was studied. The solubility of CSADP in water was determined by adding a known quantity of solute in solvent maintained at constant temperature till it is completely dissolved. Using this technique, the magnitude of the solubility of CSADP was evaluated for various temperatures and the temperature dependence of solubility of CSADP is shown in Fig.-2. From the graph it was found that the solubility of CSADP increases with increase of temperature.

Characterization Studies

The grown single crystal of CSADP was confirmed by powder X-Ray diffraction studies using Rigaku ultima III XRD diffractometer with (CuKα =1.54598 Å) radiation. Fourier transform infrared (FTIR) spectrum of CSADP crystal was recorded in the range of 400–4000 cm^{-1} by Perkin Elmer make model spectrum RX1 using KBr pellets technique. The optical absorption spectra of grown crystals were recorded in the range 190-1100 nm using Lambda 35 double-beam spectrophotometer. SEM image was taken using LEO 440 STEROSCAN (LEICA) microscope. Thermal stability and physiochemical changes of the samples were analyzed by recording the TGA and DTA spectrum using the instrument NETSZCH SDT Q 600 V8.3 Build 101, in the temperature range 0–300° C in nitrogen atmosphere at a heating rate of 20°C/min. The dielectric constant and dielectric loss of CSADP crystal were measured

using HIOKI 3532-50 LCR HITESTER in the frequency range 50 Hz –5MHz. In order to ensure good electrical contact between the crystal and the electrodes, a sample of 0.8 mm x 1.2 mm x 1.4 mm was coated with silver paint.

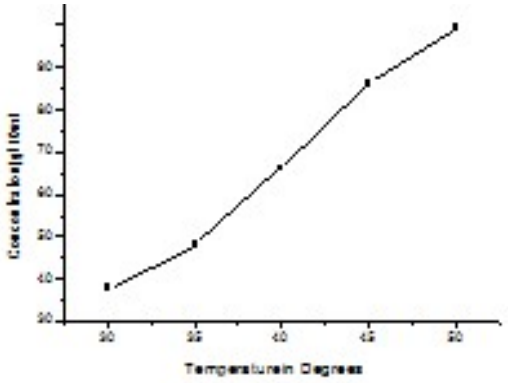

Fig.-2: Solubility Curves of CSADP Crystal

RESULTS AND DISCUSSION

Powder X-Ray Diffraction Analysis

In order to confirm the structure of the grown crystal CSADP, powder X-ray diffraction pattern was recorded and is shown in Fig.-3. Finely crushed powder of the grown crystal was used for the analysis of crystalline nature at a scan speed of 0.05^0/min. From X-ray data, the various planes were indexed using XRDA 3.1 program and the lattice parameters were evaluated. Well defined Bragg peaks are obtained at specific 2θ angles indicating that crystals are ordered with tetragonal structure. The powder XRD results reveal that the obtained diffracted peaks are similar with pure ADP crystal with slightly shifted diffraction angles. The observed prominent peaks of CSADP are (101), (200), (112), (202), (103), (312), (332), (424) but the intensities of the diffracted peaks are found to be varied. This small variation in lattice parameters may be due to the incorporation of dopants in ADP matrix.

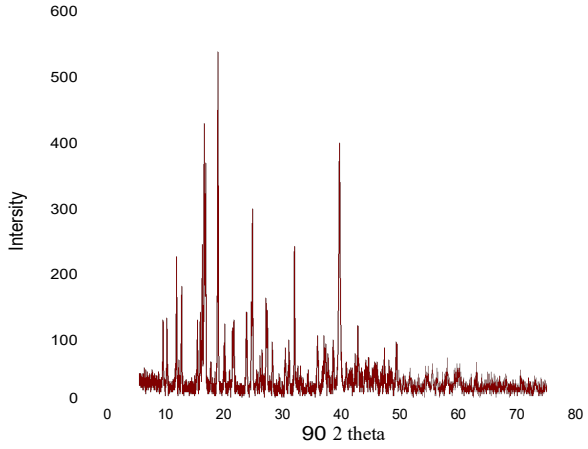

Fig.-3: XRD Pattern of CSADP Crystal

FT-IR Analysis

The room temperature mid infrared spectrum of the title compound was measured in the region 4000–400 cm^{-1} at a resolution of ±1 cm^{-1}. The FT-IR spectrum of CSADP crystal is shown in Fig.- 4. The absorption between 4000-400cm^{-1} is characterized by a broad envelope with more fine structure in the lower energy region of the envelope[23]. The NH^{3+} stretching of CSADP will be usually observed at 3300 cm^{-1} but here it is shifted to just above 3268 cm^{-1}. This shifting to lower wave number and the lower energy fine structure substantiate large hydrogen bonded association of CSADP in the crystal. In this envelope the aromatic O-H stretching vibrations at 2231 cm^{-1} are clearly evident. The peaks at

2057 cm^{-1}may be assigned to CO_2 stretching mode. The O-H bending vibrations are observed to produce intense bands at 1676 cm^{-1}. The P=O stretching also occur at 1434 cm^{-1}. The band at wavenumber 1091 cm^{-1} appears might be due to SO_3^- deformation vibration. The strong peaks at 733 cm^{-1} can be assigned to N-H bending vibration. The weak bands at 612 cm^{-1} are attributed to NH_2 and N-H wagging vibrations.

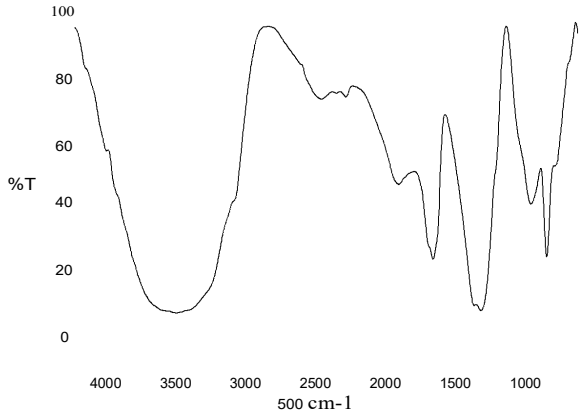

Fig.-4: FTIR Spectrum of CSADP Crystal

UV-Vis Spectroscopic Analysis

The optical transmittance spectra of CSADP crystals are recorded in the wavelength range 200-1200 nm and spectrum is shown in Fig.-5. The UV cut off wavelength of CSADP is reported as 214 nm. The transmission property of the crystal in the entire visible region suggests it suitability for second harmonic generation[24]. Hence it is clear that the presence of cobalt improves its optical transmittance and there is no considerable absorption is found in the range 481 nm to 1100 nm. This clearly indicates that the cobalt and sulphamic acid doping has increased the optical window of grown up crystal.

Vickers Hardness Test

Hardness study on CSADP crystals was carried out by static indentation test for applied loads of 25, 50 and 100g. Vicker's hardness number was evaluated from the relation:

$$H_V = 1.8544 * (P/d^2)\ kg/mm^2$$

Where, Hv is the Vicker's hardness number, P the applied loading and d the diagonal length of indentation impression in mm. The estimated hardness values of CSADP crystals for different applied load. Plot of load (P) against Vickers's hardness (H_V) is shown in the Fig.-6. It is observed that the micro hardness increases with the increase of load at lower values which can be attributed to the work hardening of the surface layers. At higher loads beyond 100gms the micro hardness shows a tendency to saturate. Significant cracking occurs which may be due to the release of internal stresses generated locally by indentation. [25,26]

Elastic Stiffness Constant

The elastic stiffness constant (C11) was calculated for different loads using Wooster's empirical 7/4 formula C11= Hv. The C11 values are shown in Table-2. These values give an idea about the tightness of bonding between neighboring atoms. The high value shows that the binding forces between the atoms were quite strong. It was calculated for the loads from 25 to 100gm. The Plot of Hv versus Elastic Stiffness Constant for the title crystal is shown in Fig.-7.

Table-1: Elastic Stiffness Constant

Load (g)	C_{11} (10^{14}Pa)
25	10.27280
50	18.66641
100	38.07316

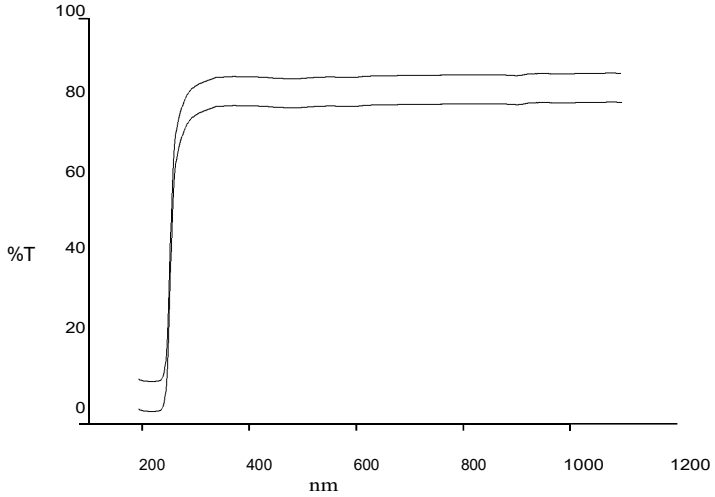

Fig.-5: UV-Vis Spectrum of CSADP Crystal

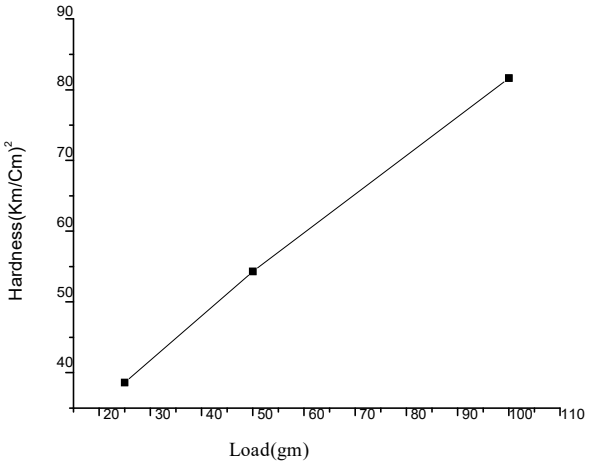

Fig.-6: Vickers Hardness Vs Load for CSADP Crystal

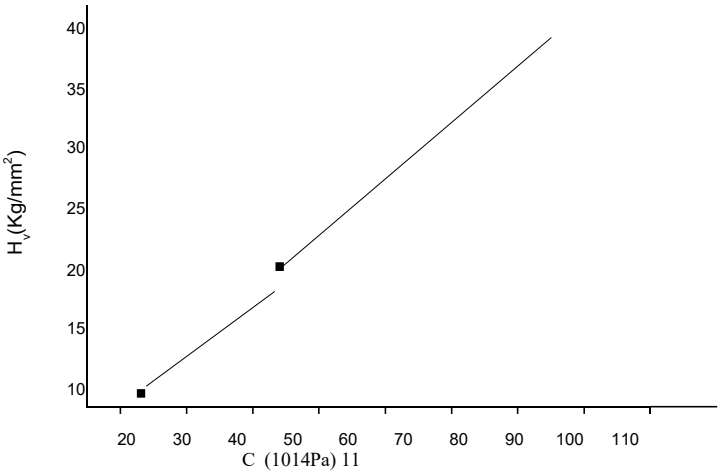

Fig.-7: Plot of H_V Versus Load of Elastic Stiffness Constant

Scanning Electron Microscopic (SEM) Studies

Since semi organic crystals are non-conducting in nature, carbon coating should be done before subjecting the CSADP crystal surface to electron beam at different magnifications. Fig.-8 depicts the

SEM image of the crystal. It shows some darker and brighter uneven areas. This might be due to solvent inclusions, which is most commonly observed in solution grown crystals. Interesting features of surface morphologies are observed in SEM, actually exhibits stepped structure.

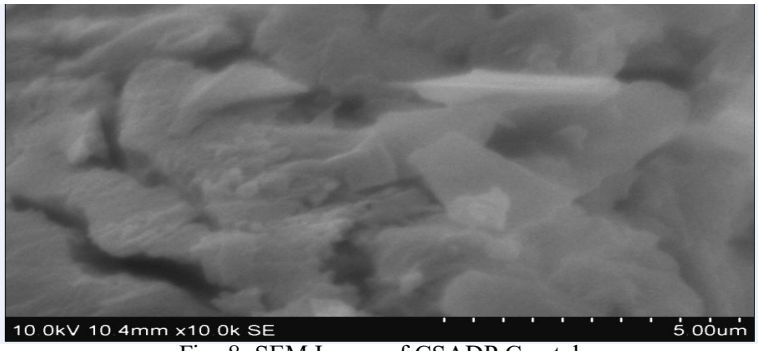

Fig.-8: SEM Image of CSADP Crystal

Thermal Analysis

Thermal stability and melting point of the material was confirmed by thermo gravimetric analysis (TGA). It was carried out using 40^0C and 1400^0C at a heating rate of 20^0C/min in nitrogen atmosphere and TGA curve obtained is shown in Fig.-9. The TGA curve shows that there is a weight loss about 60% in the temperature range 170–480^0C due to the liberation of volatile substances, probably carbon dioxide or ammonia. Prolonged heating up to 800˚C shows almost complete weight loss and the residual weight obtained at 800˚C is only about 35%.

Differential Scanning Calorimetric (DSC) Analysis

Differential scanning calorimetric (DSC) study was performed using DSC 200 PC in the temperature range 20-300^0C at a heating rate of 20˚C/min in the nitrogen atmosphere and the spectrum was shown in Fig. 10. From the figure, we understood that there is a sharp endothermic peak at around 160^0C and belongs to the melting point of the specimen. The sharpness of the endothermic peak suggests that the good crystallinity of the specimen. Hence, the compound is stable up to the melting point.

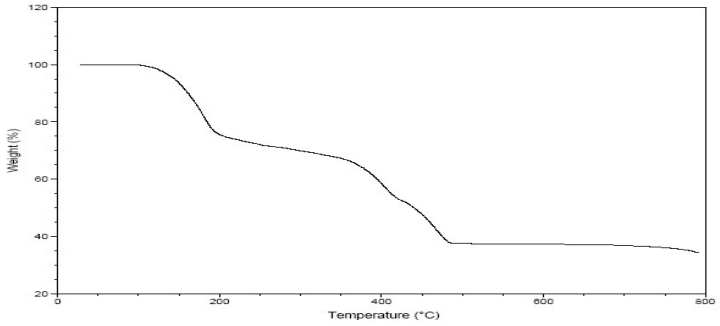

Fig.-9: TGA of CSADP Crystal

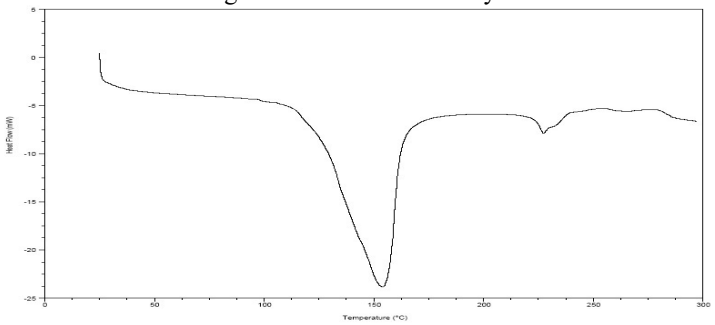

Fig.-10: DSC Curve of CSADP

Dielectric Studies

The dielectric constant of a material is generally composed of four types of contributions, viz. ionic, electronic, orientational, and space charge polarizations.[27] All of these may be active at low frequencies. The nature of variations of dielectric constant with frequency and temperature indicates the type of contributions that are present in them. The dipolar orientational effect can be seen in some materials at high frequencies and ionic and electronic polarizations below 10^6Hz. The large value of ε_r at low frequency and at low temperature is due to the presence of space charge polarization, which depends on the purity and perfection of the sample. Figure-11 shows the variation of dielectric constant with frequency measured at room temperature for the CSADP crystal. The dielectric constant is a maximum at low frequency and decreases with increasing of frequency for the crystals. The increase in the dielectric constant at low frequency is attributed to space-charge polarization. The dielectric constant decreases with increasing frequency as reported.[28]

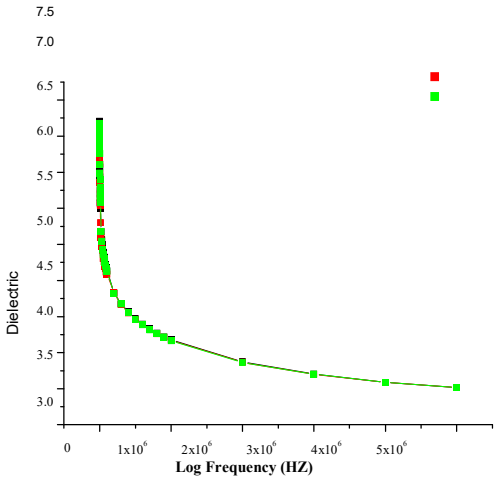

Fig.-11: Variation of Dielectric Constant with Frequency for CSADP Crystal

Nonlinear Optical Test

The SHG efficiency of CSADP was measured by Kurtz and Perry powder technique.[29] The grown crystals were characterized for their NLO property. Nd:YAG laser emits fundamental wavelength λ at 1064 nm was used. For this purpose, the output from Nd:YAG laser was used as source and it was illuminated to the crystal specimen. Pulse energy was296 mJs^{-1} and pulse width was about 10 ns. The output from the q-switched laser as focused into the crystals. The output could be seen as a bright green flash emission from the sample.

CONCLUSION

Optically good quality single crystals of CSADP were grown by low temperature solution growth method. Powder X-ray diffraction studies confirm the crystallinity and shows that CSADP crystal structure is tetragonal. The spectroscopic study was carried out with a view of obtaining an insight into the structural aspects of optical nonlinearity of crystals. Thus the molecular structure of the synthesized compound was confirmed by the spectral analysis. UV - vis spectrum show that the grown crystals were optically transparent and the lower cut off wave length found to be 214 nm, and hence the grown crystals are suitable for frequency conversion applications. The mechanical properties were examined and it was observed that, increase in hardness with the increase of load at lower values which can be attributed to the work harde ning of the surface layers. At higher loads beyond 100 gms the micro hardness shows a tendency to saturate. Significant cracking occurs which may be due to the release of internal stresses generated locally by indentation. The elastic stiffness constant (C_{11}) was calculated for different loads using Wooster's empirical formula. SEM result shows some darker and brighter uneven areas which is due to solvent inclusions, which is most commonly observed in solution growth. From TGA studies it is shown that there is a weight loss of about 60% in the temperature range 170–480^{0}C due to the liberation of volatile substances, probably carbon dioxide or ammonia. In DSC analysis it

is understood that there is a sharp endothermic peak at around 160^0C. It belongs to the melting point of the specimen. The sharpness of the endothermic peak suggests that the good crystallinity of the specimen. This may be due to the release of space charges as a result of reduction in the barrier properties of material with the rise in temperature and may be a responsible factor for the enhancement of AC conductivity of material with temperature at higher frequencies.

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