



ISSN: 2350-0328

**International Journal of Advanced Research in Science,  
Engineering and Technology**

**Vol. 3, Issue 4 , April 2016**

# **Growth and Characterization of Pure and Ammonium nickel (II) sulphate hexahydrate doped Potassium chloride Single Crystal**

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**ABSTRACT:** Single crystals of pure and Ammonium nickel (II) sulphate hexahydrate doped Potassium chloride (ANSP), an inorganic material; have been grown by slow evaporation technique using water solvent at room temperature. Single crystal X-ray diffraction study revealed that the ANSP crystal belongs to cubic system. The crystalline nature of grown pure and ANSP crystal was confirmed by powder X-ray diffraction analysis. The functional groups of the grown crystals were predicted by FTIR analysis. The UV-Vis study was performed to know the optical behavior of the grown crystals. Vickers micro hardness test was measured to find the suitability of the grown crystals for device fabrication. TGA/DTA analyses were carried out to characterize the thermal behaviour and stability of the ANSP crystal. The SHG conversion efficiency of the pure and ANSP were determined with reference to KDP using Powder Kurtz Perry technique.

## **I INTRODUCTION**

Nalwa and Miyata et al [1] have formulated a set of characteristics for a nonlinear optical material to be introduced into optical applications. The nonlinear optical material must be highly transmitting at the fundamental and harmonic wavelengths and must have a laser induced damage threshold high enough to allow optical intensities that will provide adequate conversion efficiency. Phase matching must also be possible in the material. The material also needs to be of good optical quality to provide optical transmission without distortion. Above all, the crystal must be a non-centro symmetry for SHG and have large refractive indices. Further the materials must be non-hygroscopic to introduce it into demonstrable applications and have mechanical and thermal stability. The magnitude and speed of the nonlinearities are essential characteristics in any assessment of the materials for NLO applications. i.e. fast optical response. In this perspective, the present work involves growing of as-grown bulk single crystals of pure and ANSP by solution growth technique. The PXRD of the grown crystals was carried out to know the crystal system and lattice parameters. Vibrational studies were done by recording FT-IR spectra in the range 400-4000  $\text{cm}^{-1}$ . The optical transparency was checked by using Perkin Elmer Lambda 35, UV-Vis spectrophotometer in the range of 200-1100 nm. The SHG test on the grown crystals was performed by Kurtz and Perry powder method. The micro hardness measurements were carried out using Vicker's hardness tester. The thermogravimetric (TG) and differential thermal analysis (DTA) were carried out to study the thermal property of the grown crystals.

## **II EXPERIMENTAL METHODS**

An aqueous solution of Potassium chloride and ammonium nickel (II) sulphate hexahydrate (ANS) taken in the ratio 2:1 and was stirred for 3-4 hours at room temperature to obtain a homogeneous solution. Solution was filtered using the whatman filter paper and poured into the beaker. The beaker with filtered solution was covered with a perforated lid with very small pin holes and was allowed to crystallize by slow evaporation technique at room temperature. A good optically transparent crystal were harvested in a growth period of 10 days as shown in Fig.1(a). The similar procedure was followed to grow pure KCl crystals by preparing saturated solution of KCl at room temperature. After a span of 10 days of solvent evaporation, the solution becomes supersaturated and bulk crystals as shown in Fig.1(b) were found.



Fig.1 as grown (a) ANSP (b) Pure crystal

### III RESULTS AND DISCUSSION

#### A Powder X-ray Diffraction

Pure and ANSP grown crystals were subjected to powder X-ray diffraction analysis using Bruker D8 advance diffractometer. The samples were examined with Cu  $\alpha$  radiation in a  $2\theta$  range of  $20^\circ\text{C} - 60^\circ\text{C}$ . The well defined Bragg's peaks at specific  $2\theta$  angles show good crystallinity of the material. The indexed powder X-ray diffraction patterns of pure and doped ANSH are shown in Fig.2. The characteristic peak of pure KCl is in good agreement with JCPDS file No.73-0380. The additional peak observed in PXRD pattern of ANSP doped crystal is identified as (311) plane by comparing it with JCPDS file No.72-0505 of ammonium nickel(II) sulphate hexahydrate. Hence the incorporation of the dopant in pure crystal lattice was confirmed.

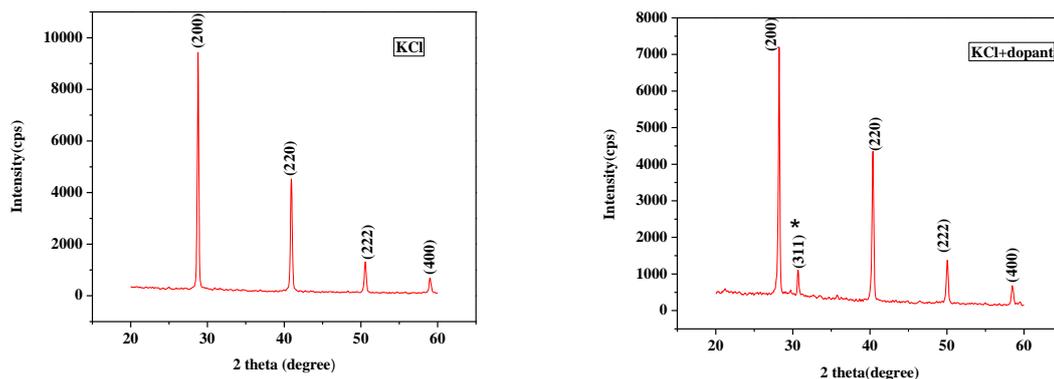
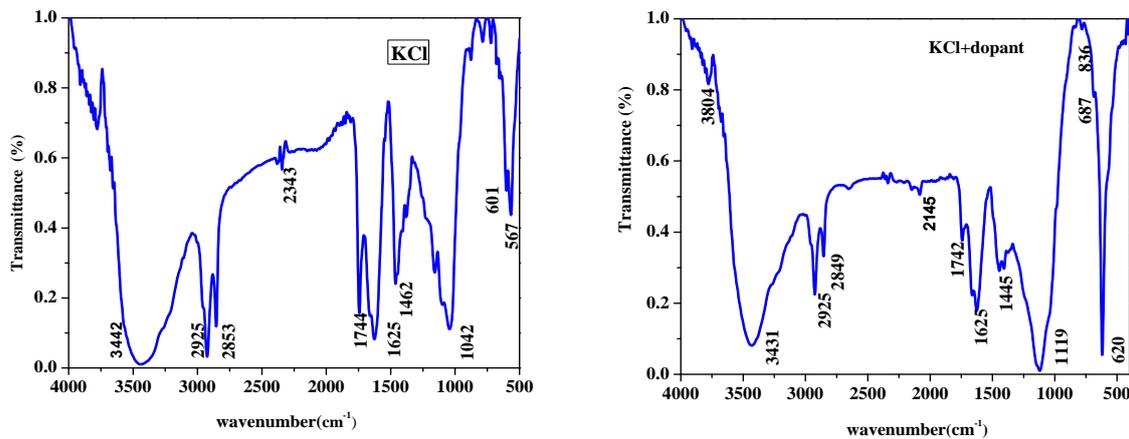


Fig.2 X-ray diffraction pattern of pure and doped crystal

#### B FT-IR Analysis

The FT-IR spectrum of KCl and ANSP crystals were recorded by using Tensor 27 Spectrometer in the region  $400-4000\text{ cm}^{-1}$  using KBr pellet technique in order to identify the functional groups present in the crystals and are shown in Fig.3 (a & b). The detailed vibrational frequency assignments are presented in Table 1. The stretching vibrations of the water molecule are expected in the region  $3000-3600\text{ cm}^{-1}$ [3]. Accordingly, the broad vibrational band observed at  $3430\text{ cm}^{-1}$  attributed to the symmetric stretching and the medium broad band noticed at  $1625\text{ cm}^{-1}$  is assigned to the bending vibrational mode of water molecule. The band observed at  $783\text{ cm}^{-1}$  is assigned to libration mode of water molecule. In the high frequency region, the band observed at  $2925\text{ cm}^{-1}$ ,  $2849\text{ cm}^{-1}$  is due to  $\text{NH}_3^+$  stretching vibrations and the peak observed at  $1418\text{ cm}^{-1}$  is due to  $\text{NH}_3^+$  bending. These assignments agrees well with

that reported [2] for Zinc Sulphate Heptahydrate. In general a free  $\text{SO}_4^{2-}$  ion has  $T_d$  symmetry and has four fundamental vibrations namely a non degenerate mode at ( $\nu_1$ ) at  $981\text{ cm}^{-1}$  a doubly degenerate mode( $\nu_2$ ) and triply degenerate vibrations ( $\nu_3$  and  $\nu_4$ ) at  $1104\text{ cm}^{-1}$  and  $613\text{ cm}^{-1}$  respectively [2]. In the light of that the peak observed at  $1119\text{ cm}^{-1}$  is attributed to the triply degenerate symmetric stretching ( $\nu_3$ ) of  $\text{SO}_4^{2-}$  mode. The band observed at  $450\text{ cm}^{-1}$  is assigned to the doubly degenerate ( $\nu_2$ )  $\text{SO}_4^{2-}$  mode. The peak appeared at  $836\text{ cm}^{-1}$  is reasonably assignable to the ( $\nu_2$ ) of  $\text{SO}_4^{2-}$  non degenerate mode. The mode at  $620\text{ cm}^{-1}$  is assigned as the triply degenerate vibrations ( $\nu_4$ ) of  $\text{SO}_4^{2-}$ . The above assignment agrees with that reported by literature [2,3]



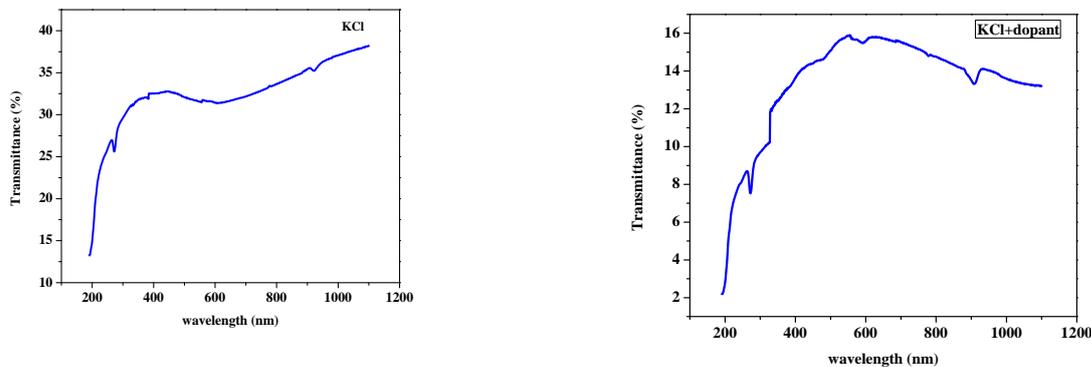
**Fig.3 FTIR spectrum of pure and ANSP crystal**

**Table 1Vibrational frequency assignments**

ANSP Frequency ( $\text{cm}^{-1}$ )	Vibrational assignments
3431	O-H stretching
2925	$\text{NH}_3^+$ stretching
2849	$\text{NH}_3^+$ stretching
1625	O-H bending
1119	$(\text{SO}_4^{2-})$ triply degenerate sym stretching
836	$(\text{SO}_4^{2-})$ triply degenerate mode
783	O-H stretching
620	$(\text{SO}_4^{2-})$ triply degenerate Vibration
450	Doubly degenerate $\text{SO}_4$ mode

### C UV –Vis-NIR analysis

Transmission spectra are quite important for any doped materials, as it is a tool to analyze the interaction between dopant and parent molecule and to know the stability for optical application. Hence the optical transmittance spectrum of the grown crystals was measured in the wave length range 200 nm to 1100 nm by Lambda 35 spectrophotometer and shown in Fig.4. From the spectrum it is observed that both the pure and ANSP crystals have a very low cut off wavelength less than 200 nm. The peaks due to considerable absorption was observed at 272 nm, 605 nm and 272 nm, 907 nm for the pure and doped grown crystals respectively, this is excepted due to the absorption of hydrated transition of metal ions. In addition to that the transmittance percentage of ANSP was reduced to half when compared to pure crystal.



**Fig.4 UV-Vis-NIR spectrum of pure and doped crystal**

### D Microhardness studies

The micro hardness of the grown crystals was measured using Shimadzu micro hardness tester with a diamond indenter. For this purpose the pure and doped crystals were well polished to avoid surface defects. The indenter time was kept as 10s for all different loads. The micro hardness number,  $H_v$  was determined from the relation  $H_v = (1.854) P/d^2$  Kg /m . Where,  $H_v$  is the Vickers hardness number (Kg /mm<sup>2</sup>), P is the applied load in (g), d is the diagonal length of the indentation impression in mm. It was observed that for both the crystals hardness value was found to increase with load, but the  $H_v$  value is less for the doped crystals for all the applied loads. For an indentation load at above 75gm, cracks were initiated in the pure crystal, where as it was happened for the load 17gm itself in the case of doped crystal. Hence the hardness value and the mechanical strength of the doped crystal is low, when compared to pure crystal. This is due to the fact that, the KCl micro particles that get into the crystal are responsible for crystal defects. This is also confirmed by calculating the work hardening co-efficient value n. The work hardening co-efficient value 'n' of the grown crystals was determined by the least square fit method. For this purpose the log-log plot drawn between 'd' and 'p', which yields a straight line. The slope of the line gives the value 'n'. The calculated value of 'n' for pure and doped crystal is 1.2 and 1.6 respectively. According to onitsch  $n \leq 2$  for hard materials and  $n \geq 2$  for soft materials [4]. Hence it is concluded that both the pure and doped crystals are belongs to the hard material, and also we can infer that pure crystal is found to be harder than doped crystal, which is also confirmed by their n and  $H_v$  values.

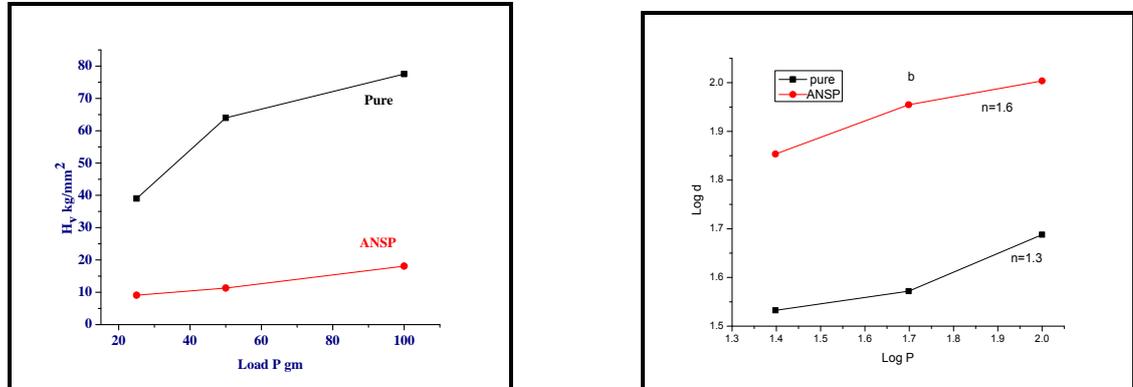


Fig. 5 Vicker's micro hardness of pure and ANSP (a)  $H_v$   $\text{kg/mm}^2$  vs load  $P$  gm (b)  $\log p$  vs  $\log d$

### E TG/DTA Studies

The thermogravimetry and differential thermal analysis of grown crystal were carried out in the temperature range  $40^\circ\text{C}$ - $730^\circ\text{C}$  with a heating rate  $20^\circ\text{C}/\text{min}$  in nitrogen atmosphere using Perkin Elmer STA 6000 model TG-DTA instrument. The thermal analysis is a very useful technique in the characterization and thermal stability of the crystal. The TGA and DTA curves of the crystal are shown in Fig.6a. The TGA thermogram reveals that the sample of the doped crystals is thermally stable upto  $103^\circ\text{C}$  and then it starts to decompose due to elimination of a water molecule from the crystal lattice. This is confirmed by small broad endothermic peak in DTA trace at  $154^\circ\text{C}$ . The major weight loss is observed in the temperature range  $281^\circ\text{C}$  -  $724^\circ\text{C}$  and is equal to  $13.75\text{gm}$ . There is no mass loss is observed between the temperature range  $222^\circ\text{C}$  -  $282^\circ\text{C}$ , and hence the crystal has a thermal stability in this temperature range also. The DSC curve (Fig.6.b) is also in consistent with above predictions.

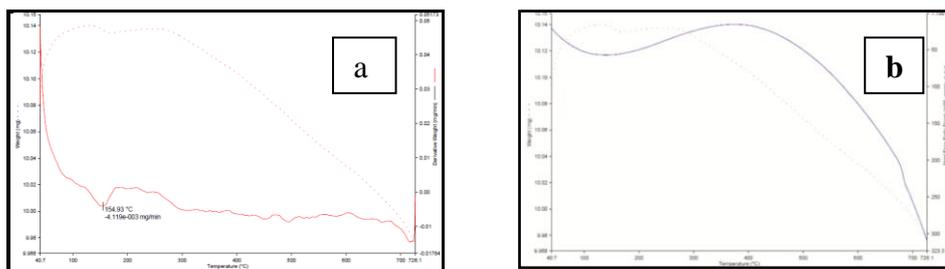


Fig.6 shows ANSP (a) TGA and DTA curves (b) DSC curve

### F Second harmonic generation test

Quantitative measurement of the conversion efficiency of the grown crystals was determined using the Kurtz-Perry powder second harmonic generation test. The SHG efficiency will vary with the particle size of the powder sample [5]. The good quality optical crystals have been powdered finely and filled in the capillary tube. This was illuminated by Q-switched Nd:YAG laser emitting fundamental wavelength of  $1064\text{ nm}$  with pulse width  $10\text{ ns}$  high intense light. The second harmonic signal generated in the crystalline sample was confirmed from the emission of green radiation of wavelength  $532\text{ nm}$  in both the crystals. The SHG efficiency were calculated with KDP as a reference material. The intensity of the SHG gives an indication of the nonlinear optical behavior of the material [6]. It is observed that the measured second harmonic generation efficiency of the pure and doped crystals is  $0.72$  and  $0.76$  times as that of KDP as shown in Table 4. So these crystals can be used for NLO applications

**Table 2 Comparison of SHG signal energy output**

Input power mJ/pulse	KDP Mv	Pure KCl	ANSP
1.0	95	69	72

#### IV CONCLUSION

The pure and ammonium nickel sulphate hexahydrate doped KCL single crystals were grown by slow evaporation method. The PXRD patterns of the grown crystals confirm the inclusion of dopant into the pure crystal lattice. The presences of functional groups were confirmed using FT-IR spectrum by identifying the peaks in their characteristic regions. In UV-vis-NIR spectra, due to considerable absorption two peaks were observed, because of absorption of hydrated transition metal ions. At the same time the transmittance percentage of doped crystal was reduced to half. In the pure and ANSP crystals, the cracks were initiated for an indentation loads of 75gm and 17gm respectively. The micro hardness number ( $H_v$ ) for pure and ANSP are 75 kg/m and 18 kg/m respectively. From these, it is concluded that the dopant decreases the mechanical strength of the crystal.. The doped crystal is thermally stable upto 103°C and under went major weight loss in the temperature range 281°C-724°C. The SHG is confirmed by Kurtz Perry test and the SHG efficiency of the pure and doped crystals is 0.72 and 0.76 times as that of KDP.

#### Acknowledgement

The authors are thankful to Prof.P.K.Das, IISc, Bangalore, India for the SHG test. They also express their gratitude to the authorities of SAIF, IIT, Chennai, India, ACIC St.Joseph's College, Trichy, India and Cochin University, STIC , Kerala, India for providing thermal analysis facilities, to undertake this study.

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