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Growth, Structural and Spectral Studies on pure and doped Ammonium Dihydrogen Phosphate (ADP) single crystals

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ABSTRACT

Single crystals of pure, hydrogen borate and potassium nitrate doped Ammonium Dihydrogen Phosphate (ADP) were grown from aqueous solutions, employing slow evaporation technique at room temperature. The grown crystals were subjected to powder X–ray diffraction studies to study their structural characteristics. FTIR spectral analysis was performed to identify the presence of various functional groups in the crystals. The UV–Visible–NIR spectral analysis was carried out to confirm the improvement in the transparency of the ADP crystal on the addition of boric acid and potassium nitrate.

Key words: ADP, Boric acid, Potassium nitrate, Crystal growth, FTIR, X–ray diffraction, UV–Vis –NIR.

INTRODUCTION

Studies on Ammonium dihydrogen phosphate ($NH_4H_2PO_4$) crystal still attracts interest because of their unique non–linear optical, dielectric, piezoelectric and antiferroelectric properties and their variety of uses such as electro-optic modulators, harmonic generators and parametric generators. Several research works have been carried out on pure and doped ADP crystals. [1–5] In recent years, efforts have been taken to improve the quality, growth rate and properties of ADP by employing new growth techniques and also by the addition of organic, inorganic and semi organic impurities.[6–8] Inorganic non linear optical materials have large optical susceptibilities, inherent ultrafast response times, and high optical thresholds for laser power. [9,10] With an aim of finding new useful materials for academic and industrial use, an attempt has been made to modify ADP crystals by adding 1 mole % by weight of hydrogen borate and potassium nitrate in the mother solution of ADP. In this work, the structural, spectral and optical properties of hydrogen borate doped and potassium nitrate doped ADP crystals against pure ADP have been studied and reported.

MATERIALS AND METHODS

Crystal Growth

Single crystals of pure and doped ADP were grown from supersaturated solution at room temperature by natural evaporation process using AR grade samples of ADP, hydrogen borate and potassium nitrate. The dopants were added separately with pure ADP solution, each in definite molecular ratio, namely ADP: X (X being dopant) in the molar weight 1:0.01ratio. Each solution was stirred for three hours using magnetic stirrer and filtered using Whatman filter paper. The filtered solution was transferred to borosil glass beaker. It was porously sealed and placed in a dust free atmosphere for slow evaporation. The pH of the solution was noted as 4. The grown crystals were harvested after a period of 30 days. All the grown crystals were colourless, stable and transparent. Figure 1, 2 and 3 show the as grown crystals of pure and doped ADP. The crystals were characterized using FTIR, UV-VIS-NIR spectroscopic techniques and powder XRD technique.

Characterization

The FTIR spectra of pure, hydrogen borate doped and potassium nitrate doped ADP crystals were recorded by KBr pellet technique using Perkin Elmer FTIR Spectrophotometer in the range 4000-400 cm^{-1} at St. Joseph College, Trichy. Powder X-ray diffraction pattern was recorded using a Philips X pert PRO X-ray diffractometer with CuKα (λ=1.5418Å) radiation at University of Madras. The optical properties of the grown crystals were studied using Shimadzu UV-1601 visible spectrometer in the wavelength region 200-1100 nm at Ethiraj College, Chennai.

RESULTS AND DISCUSSION

FTIR Spectroscopic study

In the present work, FTIR spectra of pure and doped ADP crystals were compared and the complete vibrational band assignments were carried out. The comparative FTIR spectral studies confirm the presence of borate ion and the nitrate ion in the respective doped crystals. In the present work, the FTIR spectra of pure and doped ADP single crystals were presented in Figures 4, 5 and 6 respectively.

In spectrum of pure ADP, the broad band around 3250 cm^{-1} was due to the O-H vibrations of water, P-O-H group and N-H vibrations of ammonium. The band at 2387cm^{-1} was assigned to hydrogen bond. [11] The broadness was due to the hydrogen bonding interaction with adjacent molecules. The O-H bending vibration gave the peaks at 1706, 1642cm^{-1}. The peak at 1409cm^{-1} was due to the bending vibration of ammonium. The very strong band at 1292cm^{-1} was due to the combination of the asymmetric stretching vibration of PO_4 with lattice. The peaks at 1098 and 910cm^{-1} represented P-O-H vibrations. The medium bands at 560, 405cm^{-1} were due to PO_4 vibrations.

In the spectrum of hydrogen borate added ADP crystal, the band appearing at 3100cm^{-1} included O-H vibrations of water and N-H vibrations of ammonium. [10] The sharp peaks at 1292 and 1409cm^{-1} in the spectrum of ADP were shifted to 1288 and 1417cm^{-1} and they became medium intensity bands due to the presence of borate ion. The peak at 1417cm^{-1} was due to B-O terminal asymmetric stretching and the symmetric stretch of B-O vibrations lied in the region 910cm^{-1} and 1100cm^{-1}. [9] The peak at 1706cm^{-1} in pure ADP due to bending of water has broadened and has become a medium intensity band at 1697cm^{-1}, showing that the moisture content has been lost due to the addition of boric acid in the ADP crystal.

In the FTIR spectrum of potassium nitrate added ADP crystal, there was a shift in the peak positions of P-O-H and PO_4 vibrations compared to the pure ADP crystal. Also the inorganic nitrate salts exhibit a very strong band at 1410-1350cm^{-1} due to asymmetric NO_3 stretching. [12] Here the presence of a very strong band at 1403cm^{-1} indicated the presence of nitrate ion in the lattice of the potassium nitrate doped ADP crystal. Also the bands due to hydrogen bonding had a change and were present at 2452 and 2358cm^{-1} in the doped crystal. Table 1 represents the FTIR vibrational band assignments of the pure and the doped ADP crystals.

Powder XRD Analysis

Powder X-ray diffraction study was conducted to verify the single phase nature of the samples. Figures 7 and 8 show the powder XRD patterns of hydrogen borate and potassium nitrate doped ADP crystals. Well defined Bragg peaks were obtained at specific 2θ angles indicating that crystals were ordered. The powder XRD studies were done at University of Madras using SEIFERT JSO Debyeflex 2002 model X-ray diffractometer. The X radiation used was copper (K-Alpha 1) radiation (λ=1.54056Å) operating at a voltage of 40 KV and a current of 20 mA. The scanning rate was maintained at 1.6°/min over a 2θ range of 10-70° employing the reflection mode for scanning.

The figures 7 and 8 indicate the sharp peaks and hence the crystalline nature of the grown crystals. There is a slight shift in the diffracted peaks in the XRD pattern of potassium nitrate added ADP crystals. When compared to that of pure ADP, the intensity of the diffracted peaks was found to vary in both the XRD patterns of doped ADP crystals. However, there were no other phases emerging besides the tetragonal system. The powder XRD showed that the original tetragonal structure is maintained and the boric acid and potassium nitrate have entered into the lattice of ADP crystal.

Figure 1 Photograph of as grown pure ADP crystal

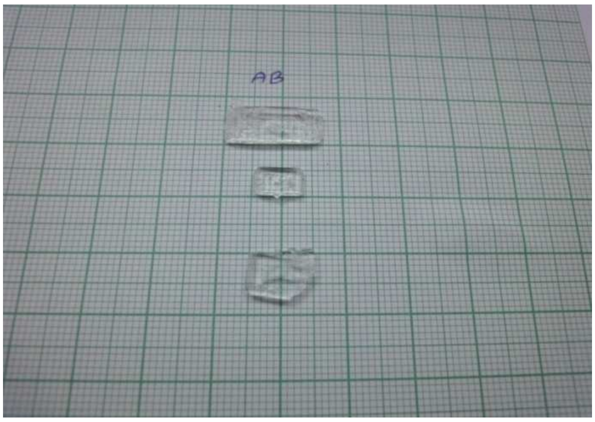

Figure 2 Photograph of as grown hydrogen borate doped ADP crystal

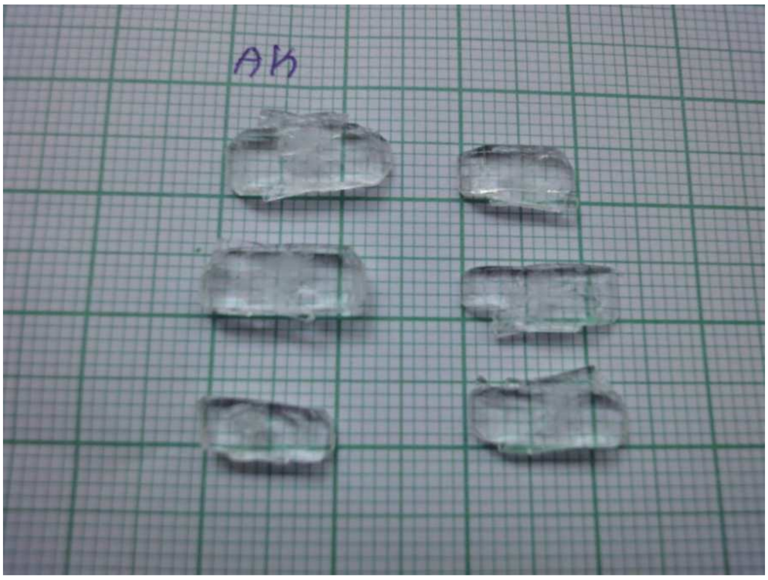

Figure 3 Photograph of as grown potassium nitrate doped ADP crystal

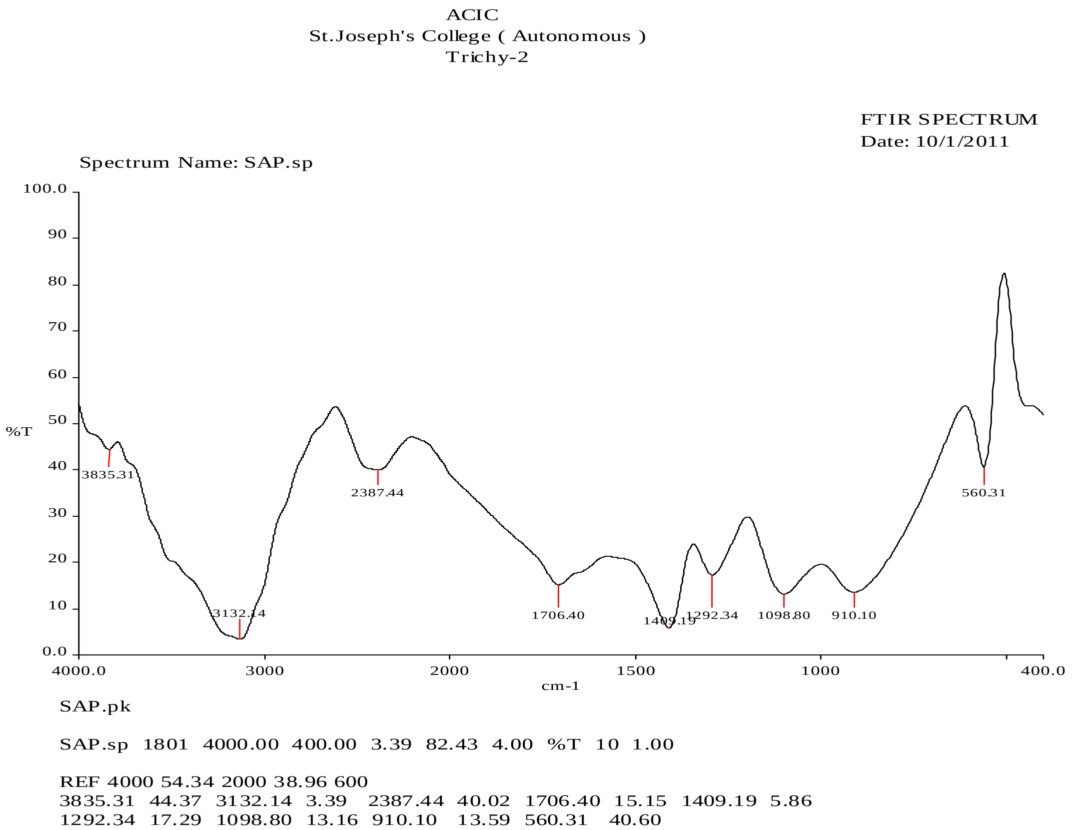

Figure 4 FTIR spectrum of pure ADP crystal

Optical transmission Spectral Studies

Single crystals of ADP are mainly used for optical applications. The study of the optical transmission range of the grown crystals is thus very important. Pure, hydrogen borate doped ADP and potassium nitrated doped ADP crystal plates with a thickness of 2mm without any antireflection coating were cut and used for optical measurements. The UV-Visible-NIR transmission spectra were recorded using Shimatzu UV-Visible Spectrophotometer in the range 200nm to 1200nm. From the spectra in the Figure 9, it was observed that both the doped ADP crystals and pure ADP crystals showed good transmittance in the entire visible and NIR regions. The overlay UV-Vis NIR spectra clearly shows that, the addition of hydrogen borate and potassium nitrate have enhanced the optical quality of ADP crystals. [13] Both the doped ADP crystals have minimum absorption in the entire region between 200-1200nm.

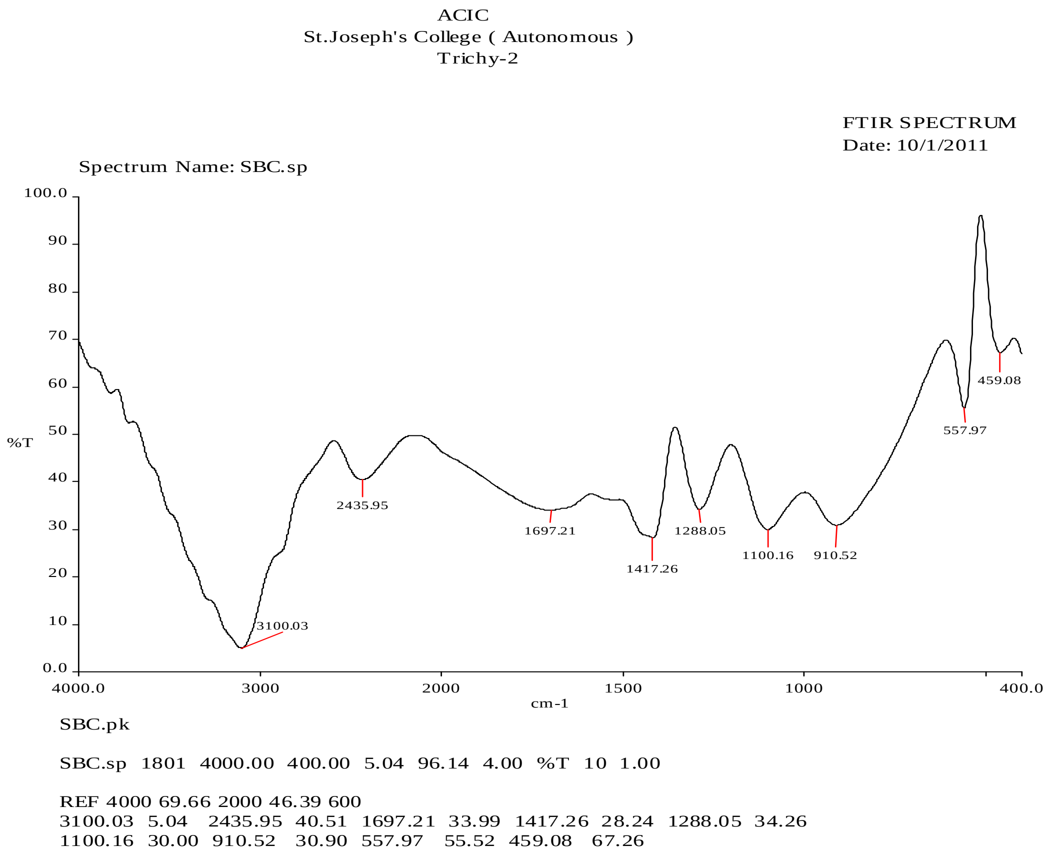

Figure 5 FTIR spectrum of hydrogen borate doped ADP crystal

Table 1 Vibrational band assignment of pure and doped ADP single crystals.

FTIR Frequency (cm^{-1})			Band Assignment
Pure ADP	Hydrogen borate doped ADP	Potassium nitrate doped ADP	
3132	3100	3133	O-H stretching, P-O-H stretching, N-H vibrations of Ammonium
2387	2435	2452 2358	Band due to hydrogen bond
1706	1697	----	O-H bending vibration
1642	----	1639	O-H bending water
1409	1417	1403	Bending vibration of ammonium
1292	1288	1302	Combination of the asymmetric Stretching vibration of PO_4 with lattice
1098	1100	1098	P-O-H vibrations
910	910	904	P-O-H vibrations
560	557	552	PO_4 vibrations
460	459	452	PO_4 vibrations

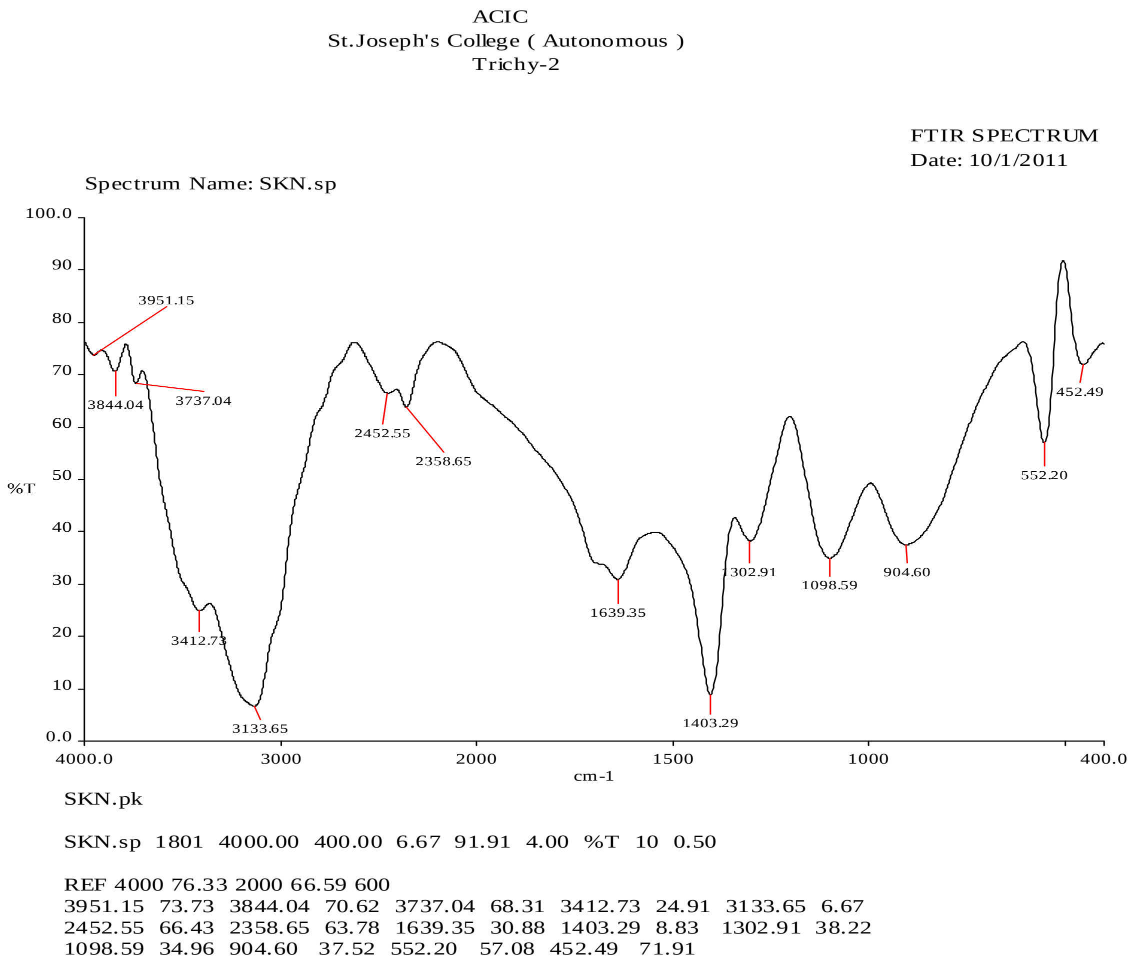

Figure 6 FTIR spectrum of potassium nitrate doped ADP crystal

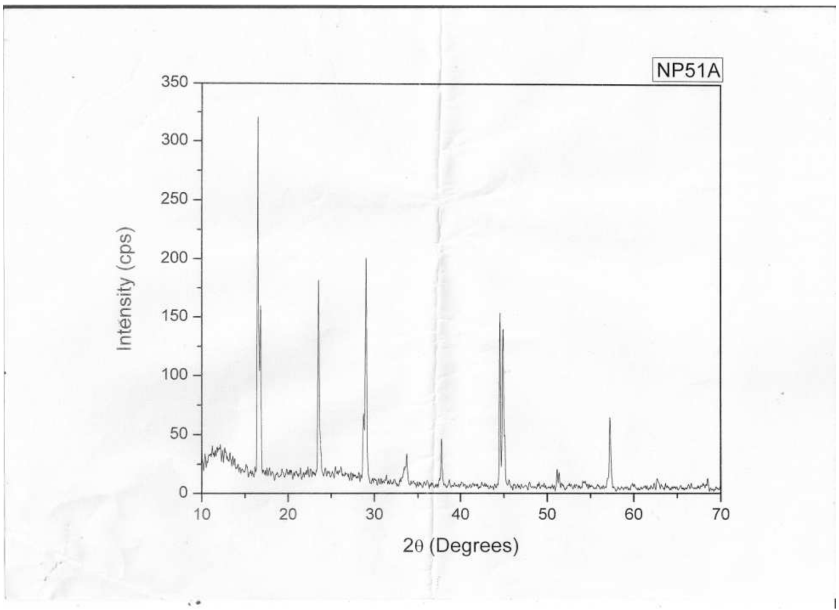

Figure 7 Powder XRD of hydrogen borate doped ADP crystal

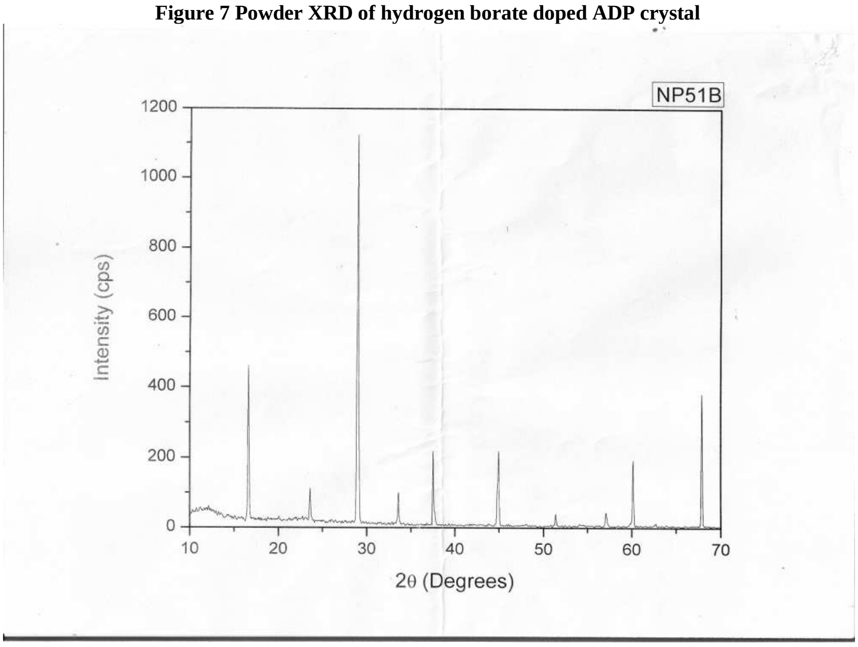

Figure 8 Powder XRD of potassium nitrate doped ADP crystal

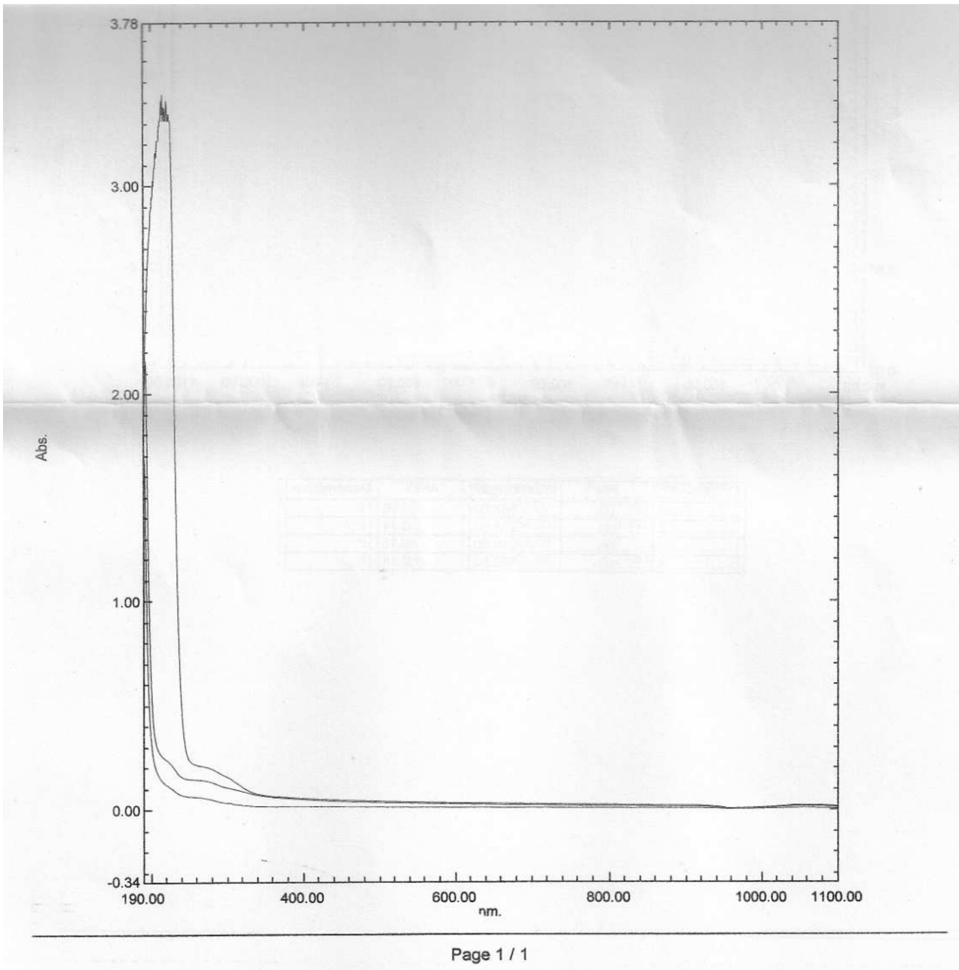

Figure 9 Overlay UV–Visible–NIR spectra of pure and doped ADP single crystals

CONCLUSION

The effect of hydrogen borate and potassium nitrate dopants on the growth of ADP from supersaturated solutions has been investigated experimentally by measuring optical trans- mission, functional groups and X ray diffraction measurements. The presence of dopants in ADP solution was found to increase the optical transmission. The enhancement of optical transmission of doped ADP crystals highlights their prospects of application as NLO materials.

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