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Growth and characterization of p- dinitroaniline doped KDP single Crystal

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ABSTRACT

Potassium dihydrogen phosphate (KDP) is an excellent inorganic nonlinear optical material with different device applications. In the present work, single crystals of pure and p-dinitroaniline doped KDP crystals have been grown from the aqueous solution by slow evaporation technique. The grown crystals have been subjected to various characterizations studies like UV-visible, FTIR spectroscopy, x-ray diffraction, SEM, EDAX and dielectric studies. FTIR spectrum analysis confirmed the presence of p- dinitroaniline in KDP crystals. UV- visible studies suggest that the crystal is suitable for nonlinear applications. Dielectric studies confirmed the single phase and high purity of the crystal.

INTRODUCTION

Great efforts have been made to the research and design of highly efficient nonlinear optical (NLO) materials due to widespread applications such as high speed information processing, optical communication and optical data storage [1]. The rapid development of the optical communication systems has led to search for more efficient compounds for the processing of optical signals. In last decade, however this effort has brought its fruits in applied aspects of nonlinear optics. The aim is to develop materials presenting large nonlinearity and satisfying at the same time all the technologies requirements for applications such as wide transparency range, fast response and high damage threshold.

Potassium dihydrogen phosphate (KDP) is an excellent inorganic nonlinear material and has considerable interest among several research workers because of its wide transparency range and high efficiency of frequency conversion, high damage threshold against high power laser. With the aim of improving the SHG efficiency of KDP crystal, researchers have attempted to modify KDP crystals either by doping different types of impurities or changing the growth conditions [2-9]. Amino acids have very large optical nonlinearity, assigned to the chiral structure, used by many workers to improve the NLO, optical, thermal and mechanical properties of KDP using as a dopant [12-13]. We try to doped p-dinitroanaline in KDP crystal in order to improve efficiency and crystal quality. The delocalised π-electrons of p-dinitroaniline is responsible for the high SHG efficiency of p-dinitroaniline doped KDP crystals.
In present work to further enhance the NLO property of KDP crystals an attempt is made to grow KDP crystals from the aqueous solution added with 0.5M%, 1M%, and 2M% p-dinitro-aniline. There was a increase in the quality of KDP crystal in presence of p-dinitroaniline.

Crystal growth
Single crystals of pure KDP and doped KDP were grown by slow evaporation of the saturated aqueous solution at 32 ^{0}C. analytical reagent grade (AR) samples of potassium dihydrogen phosphate and p- dinitroanilinewith doubled distilled water were used for the growth of single crystals. A solution of KDP and p-dinitroaniline were prepared as 0.5M%, 1M% and 2M% using water as a solvent. The P^H of the solution was 4. Each solution was stirred using magnetic stirrer at 30^{0}C for about 2 hours and then filtered using Whatman Filter paper and the filtered solution

were kept of slow evaporation in constant temperature bath at 32^0 C. After a period of 14 days transparent, colourless crystals were Harvested.Figuure1,2and3shows the grown crystals.

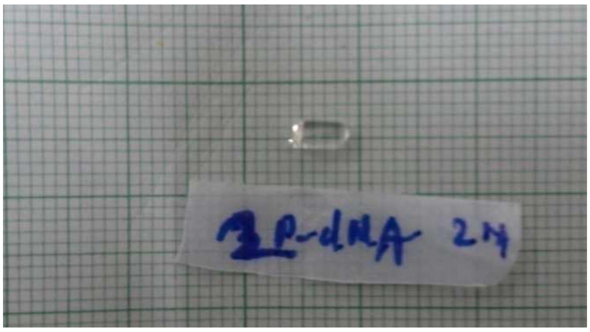


Figure 1K2M% p-DNA crystals

Figure 2K1M%P-DNA

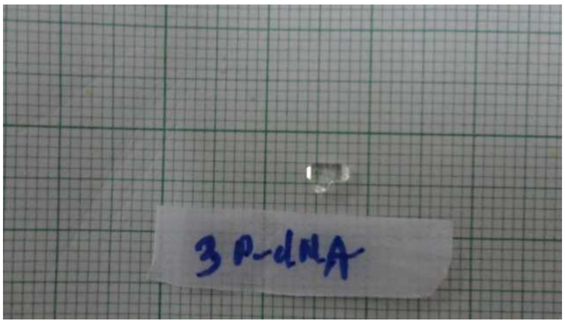


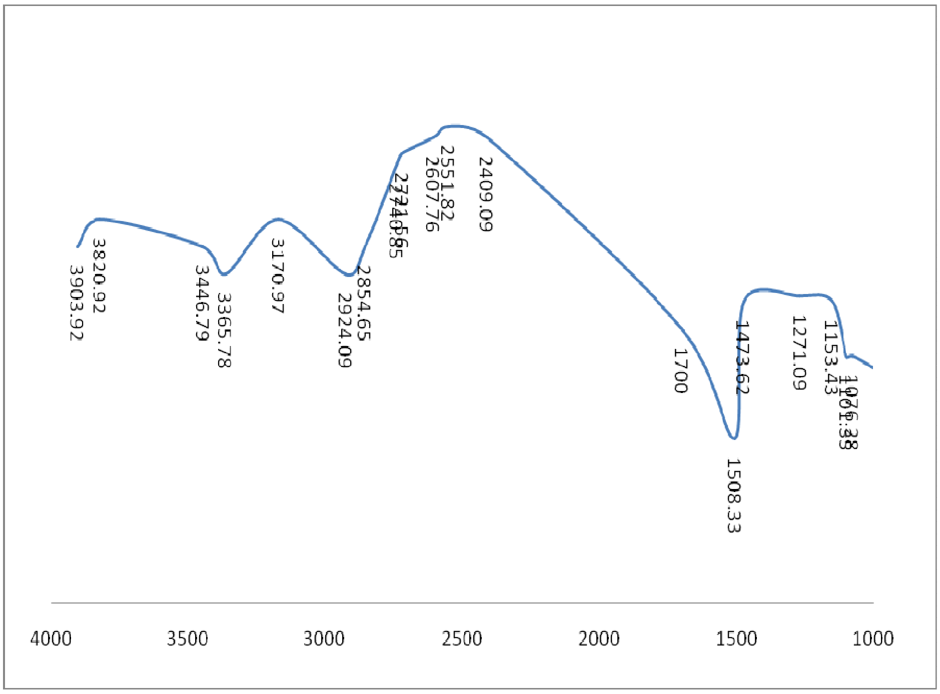
Figure 3 K3M% p-DNA

3. Characterization studies

3.1 FTIR spectral studies

Fourier transfer spectra were recorded at room temperature in the range of 4000-400 cm^{-1} as KBr pellets using Shimadzu. The recoded spectrum is as shown in fig 4,5.

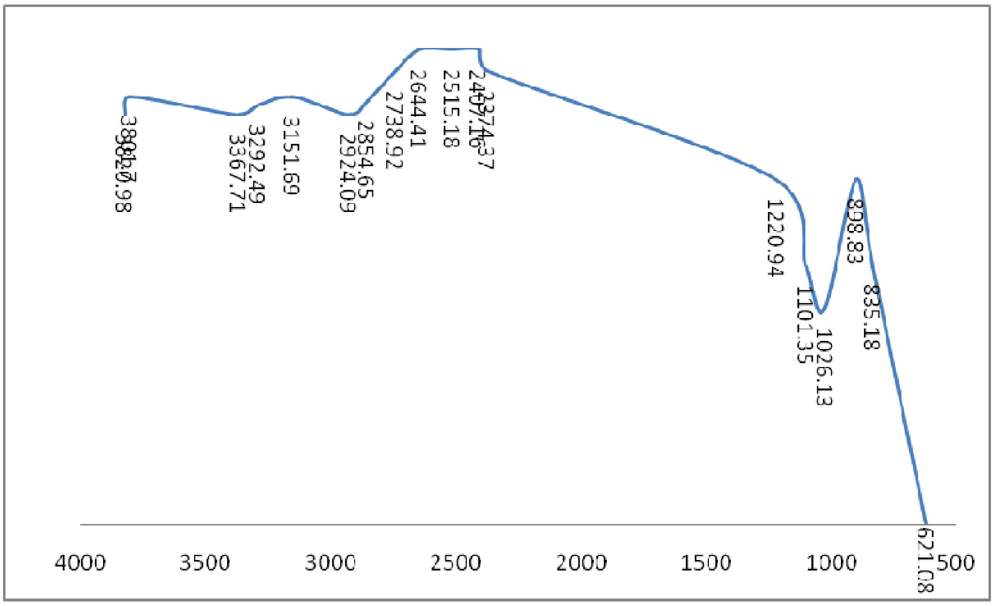
For K0.5P-DNA single crystal 3820cm^{-1} is due to free O-H stretching hydrogen bonded of KDP. 3903, 3446, 3170 are the extra peaks in the spectrum indicate the presence of p-dinitroaniline in KDP. Peaks at 3170 cm^{-1} is due to the C-H stretching. 2740cm^{-1} is for P-OH asymmetric stretching, 2409cm^{-1} for P-OH bending of KDP. 898 and 503cm^{-1} are due to the P-OH stretching and HO-P-OH is bending respectively. For K2MP-DNA single crystal extra peaks are observed at 3367, 3292, 3151, 2924, 2854cm^{-1}. 2854 cm^{-1} is due to the C-H stretching. Extra peaks indicate the presence of p-DNA in doped crystals. More extra peaks are observed in K2MP-DNA as compared to the 0.5MP-DNA that means nonlinearity increased with increase of concentration of dopant.



T ↑

Wave number cm-1→

Figure 4 FTIR spectrum of K0.5M%PDNA



%T↑

wave number cm-1→

Fig 5, 2m % pDNA

3.2 UV-Visible Spectroscopy

Figure shows that the UV-Visible spectrum of both pure and doped crystals. For optical applications, the crystal should be highly transparent in the considerable region of wavelength [10]. The good transmission of the crystal in the entire visible region suggests its suitability for second harmonic generation devices [11]. The UV-visible spectral analysis shows that both the crystals are transparent in the entire visible region.There is a strong absorption near the wavelength of 227 nm, which is slightly shifted to higher wavelength side from the pure KDP and it may be assigned to the electronic transition in p-DNA doped KDP crystals. The absence of absorption and excellent transmission in entire visible region makes this crystal a good candidate of the opt-electronic applications [9-11].

Percentage of transmission increases with the dopant in KDP crystal and the lower cut off wavelength also increase with the concentration of dopant. Figures show the UV-Visible spectrum of pure and 2M%p-DNA doped KDP crystal.

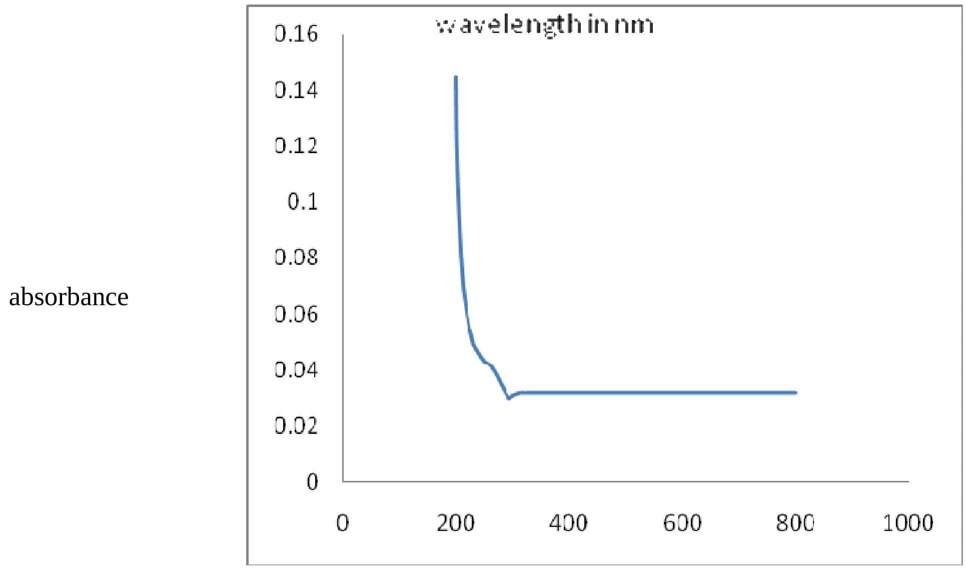


Figure 6.14 UV-Visible spectra of pure KDP

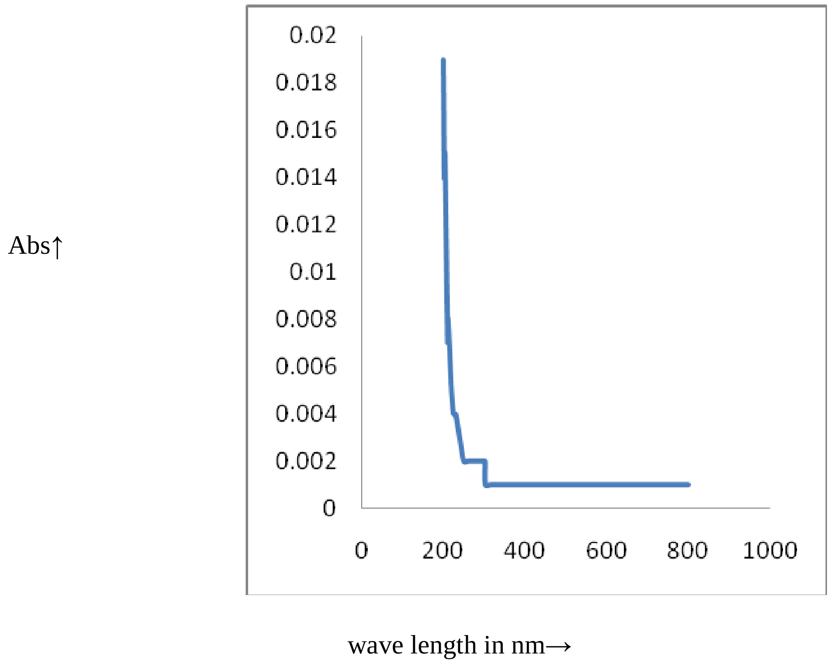


Figure 6.15 UV-Visible spectra of K2M% p-DNA

3.3 Dielectric studies:-

The dielectric analysis is an important characteristic that can be used to fetch knowledge based on the electrical properties of a material medium as a function of temperature and frequency. Based on this analysis, the capability of strong electric charges by the material and capability of for transferring the charges can be assessed. Dielectric properties are correlated with the electro-optic property of the crystals particularly when the crystals are no conducting [12]. The lower value of dielectric constant is very important parameter for enhancement of SHG efficiency. Dielectric constant measured by LCR meter having range 100Hz to 10 KHz.The dielectric constant for K0.5MP-DNA is 59.68, 48.9 and 47.77 at 100Hz, 1 kHz and 10 KHz respectively. The dielectric constant for K1Mp-DNA is 116.3, 70.77 and 65.92 respectively for frequencies 100Hz, 1 KHz and 10 KHz. These measurement shows that the dielectric constant is having lower value at low concentration of p- DNA in KDP. In both the cases the dielectric constant decreases with increase in frequency.

3.4 Powder SHG measurement:-

The SHG studies were carried out in pure KDP and doped samples. The single amplitude in mili volts indicates the SHG efficiency of the sample. Authors have observed second harmonic signals of 71mV (pure KDP) and 96.56K1M%p-DNA. It shows that doping of p-DNA in definite ratio enhances the SHG efficiency. Due to substantial number of defects formed due to the doping, one can expect an enhancement of SHG signals.

Table 6.2 SHG measurements

Name of crystals	Measured output	SHG efficiency
Pure KDP	71mV	1
K1M%G	96.56mV	1.36
K1M%p-DNA	93.72mV	1.32
K3M%p-DNA	35mV	0.45

3.5 XRD Study of pure and p-DNA doped KDP crystals

Pure and doped KDP crystals were subjected to powder X-ray diffraction studies. X-ray powder diffraction pattern of the grown crystals was obtained using XPERT-PRO X-ray diffract meter with Copper (K alpha 1) radiation of wavelength 1.54056 A^0. The powder X-ray diffraction pattern p-DNA doped crystals are shown in figures. The calculated unit cell parameters for pure KDP crystals are a=b=7.450A^0 c=6.985A^0 $\alpha=\beta=\gamma=90^0$ and volume = 388.142(A^0). The well defined, sharp peaks in the XRD patterns signify the good crystalline and single phase nature of p-DNA doped KDP crystals. There is change in intensity with slight shift and in the reflection peaks of the doped crystals compared to the pure crystal, which results in small variations in the cell parameters with slight distortion in structure; this may be attributed to the strains due to substitution of organic impurity into the KDP crystal lattice [31].

The lattice parameters calculated for K3M%p-DNA are a=b=7.21A^0 and c=8.33A^0 and volume of the unit cell of the doped crystal is 433.02$(A^0)^3$

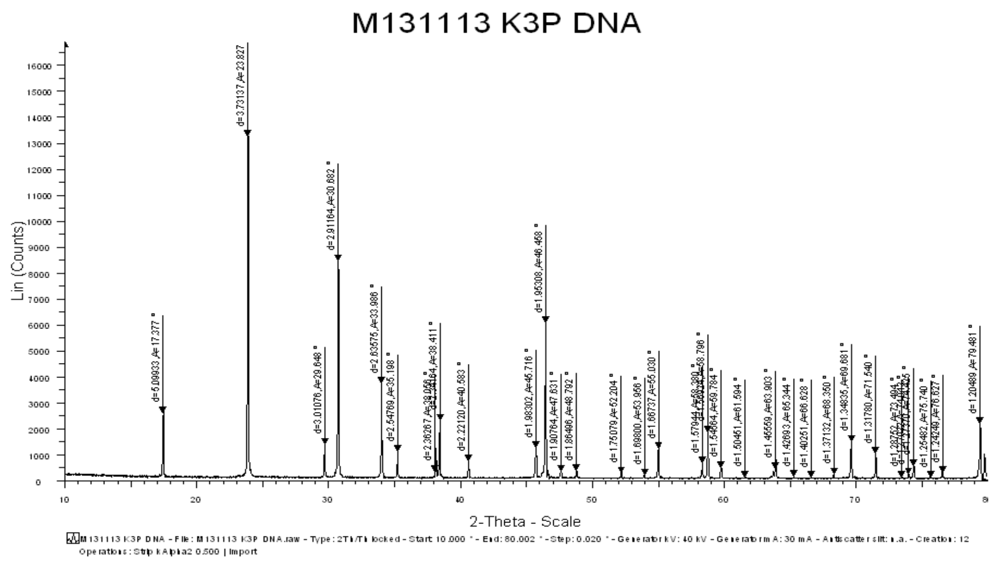


Figure 6.12 XRD diffraction pattern of K3M%p-DNA

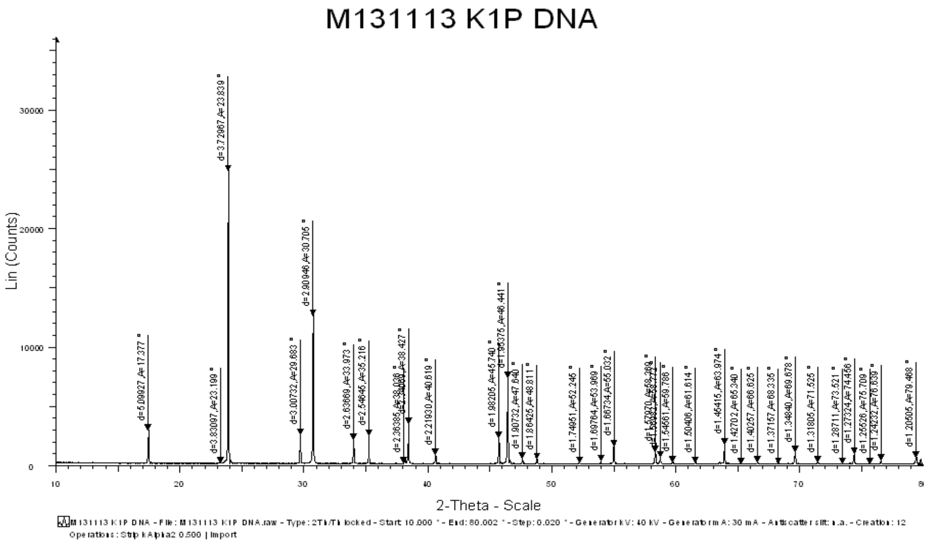


Figure 6.13 XRD diffraction pattern of K1M%p-DNA

3.6 EDAX STUDY

Energy dispersive X-ray analysis (EDAX) used in conjuction with all types of electron microscope has become an important tool for characterizing the elements present in the crystals.

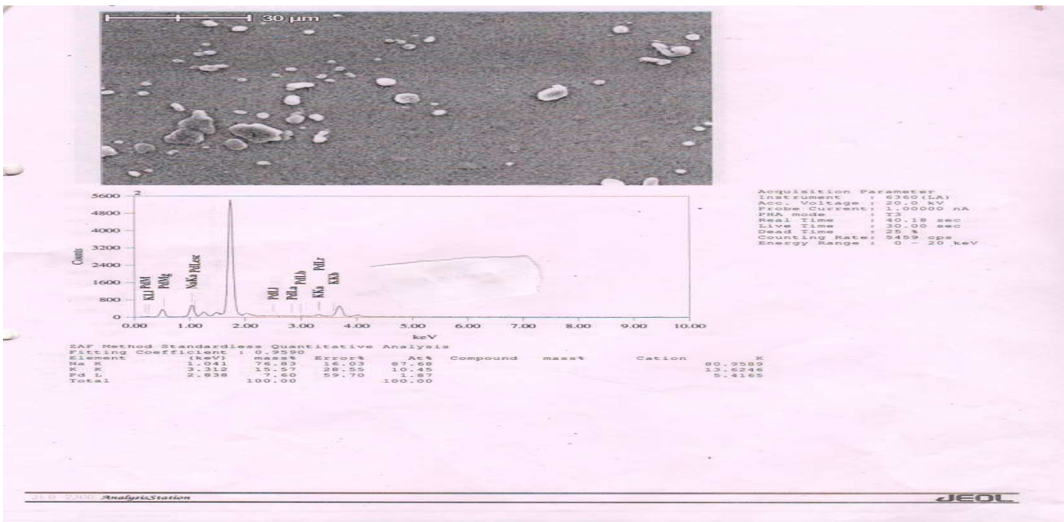


Figure 6.16 EDAX analysis and SEM image of A0.5P-DNA

In order to confirm the presence of p-DNA, the sample of the grown crystals were subjected to energy dispersive X-ray analysis using JEOL6360 scanning electron microscope. The recorded EDAX spectrum is shown in figures. SEM images of the p-DNA doped KDP single crystals suggest that the low concentration of dopant enters in the matrix of KDP crystal while the high contraptions does affect the transparency and damage threshold of grown crystals.

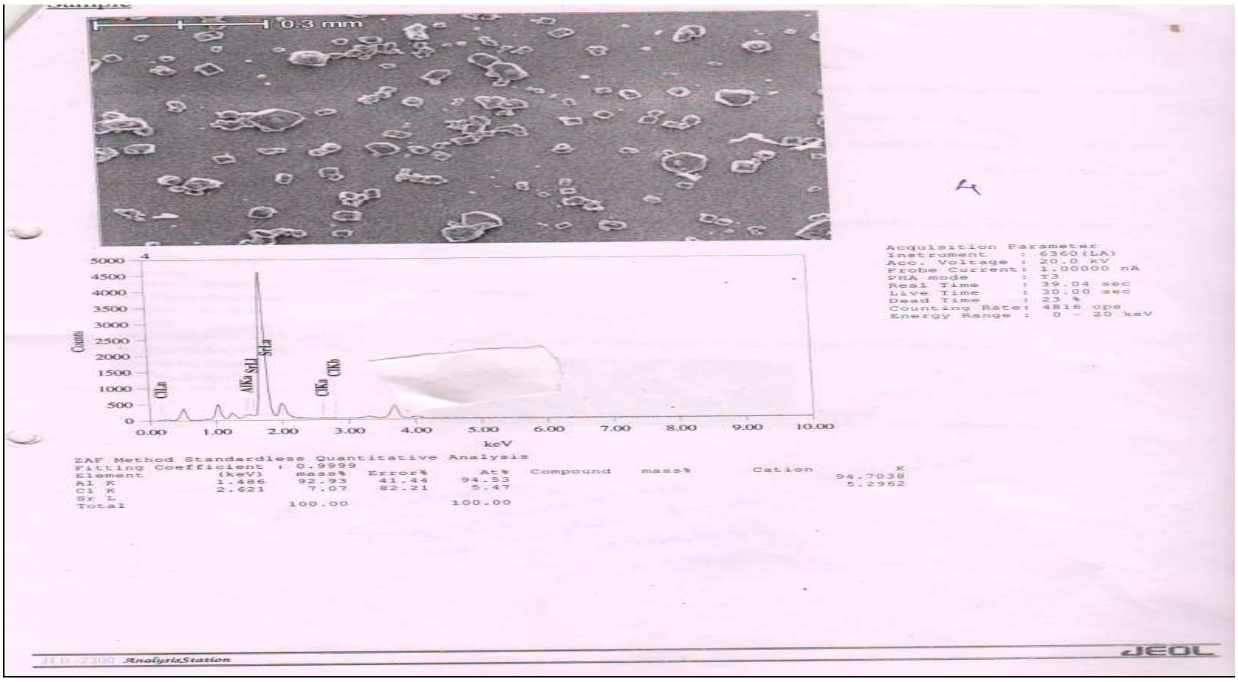


Figure 5.17EDAX analysis and SEM image of A2Mp-DNA

CONCLUSION

Transparent and colourless single crystals of pure and p-DNA doped KDP were grown by slow evaporation technique at 32 ^{0}C. Powder X-ray diffraction studies confirmed that the dopant has gone into the lattice of the crystal, but doping concentration may not accepted by KDP,so formation of grain boundaries.This study reveals slight distortion in the unit cell. The FTIR study confirms the presence of p-DNA in doped crystals. Transmission spectra reveals that doped crystals have sufficient transmission in the entire visible (200nm- 800nm) and IR regions. It has been observed that the addition of p-DNA enhances the SHG efficiency. The dielectric study reveals that p-DNA addition reduces the dielectric constant value of KDP crystals.

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