Research Article

# Growth and Characterization of Organic NLO Crystal Al Doped 2-Hydroxy Benzyledene Aniline by Slow Evaporation Method

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**Abstract**

Single crystals of Aluminium doped 2 Hydroxy benzyledene aniline was grown using ethanol as a solvent by natural evaporation method. The Grown Aluminium doped 2-Hydroxybenzyledene aniline crystals were characterized by UV-Vis spectroscopy, FTIR spectroscopy, single crystal XRD, Powder XRD, EDAX, Kurtz Perry test and Vickers micro Hardness test. The experimental results suggest the suitability of the grown crystal for opto electronic application.

**Keywords:** crystal growth UV-Vis spectroscopy, FTIR, Powder XRD studies, Vickers Hardness test

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## Introduction

Materials with large nonlinear optical characteristic are of recent interest in the area of harmonic generation and optical modulation. In current years, some polar organic crystals, which form a non-centrosymmetric structure exhibit second –order nonlinear optical properties that far surpassed those of the conventional materials has led to the synthesis and evaluation of a wide range of potentially useful solids [1]. Materials having high optical non linearity have potential applications in signal transmission, optical modulation, optical switching, data storage, displays, inflorescence, photolithography, remote sensing, chemical and biological species detection, laser printing etc [2]. Organic nonlinear materials are attracting a great deal of attention, as they have large optical susceptibilities, inherent ultra fast response times and high optical thresholds for laser power compared with inorganic materials [3,4] Organic molecules with significant non linear optical activity generally consist of a $\pi$- electron conjugated structure. In this paper, we report the growth of Aluminium doped 2-Hydroxy benzyledene aniline single crystals by slow evaporation solution technique and to study its characterization.

## Materials and Methods

### *Synthesis*

The starting material was synthesized by taking 2-Hydroxy benzyledene aniline[2HBA] and Aluminium Nitrate[AN] in a 3:1 ratio. The calculated amount of 2-Hydroxy benzyledene aniline was first dissolved in acetone. Aluminium Nitrate was then dissolved in deionized water. The dissolved HBA and AN was added and stirred continuously using magnetic stirrer for 3 hrs. The salt was obtained when the prepared solution was allowed to evaporate at room temperature. Slow evaporation technique. The synthesized salt was again dissolved in ethanol and then then allowed to crystallize by slow evaporation technique at room temperature. After a growth period of three week brown colour crystals harvested. **Figure 1** shows the photo graph of the crystal.

## Characterizations

### *Single crystal XRD*

The single crystal x-ray diffraction is recorded with the Bruker KappaAPEXIII Instrument and the wavelength of X-ray used was 0.7093A$^{o}$. It is observed from the X-Ray Diffraction data that the compound 2HBA is crystallized in

orthorhombic system with Fdd2 space group. The lattice parameters a= 12.8807A$^{O}$, b= 27.995A$^{O}$, c=5.9377 Å, α= β= γ=90.00$^{O}$ and V=2141.1 Å$^{3}$. The molecule is nearly planar. **Figure 2** shows the ORTEP Plot of the 2HBA compound.


**Figure 1** shows Al doped HBA crystal

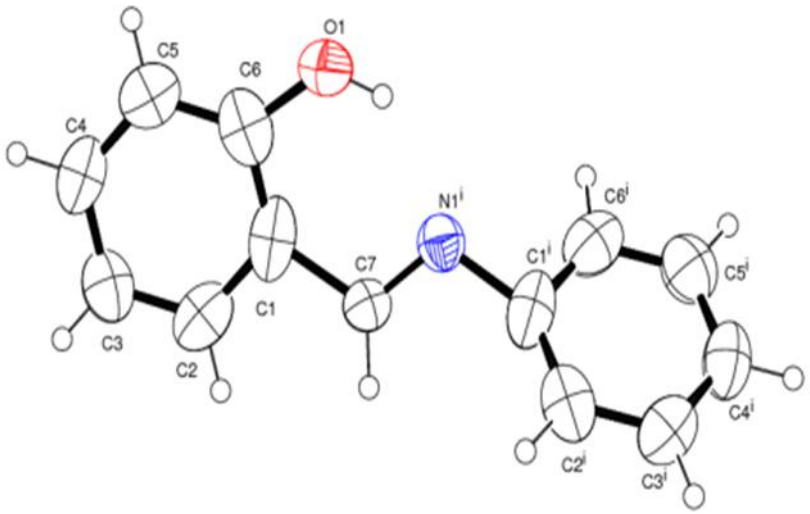


**Figure 2** HBA ORTEP

***Powder X-Ray Diffraction***

X-ray diffraction technique is a powerful tools to analyses the crystalline nature of the materials. If the material to be investigated is crystalline, well defined peaks will be observed. Powder X-Ray diffraction analysis was carried out by using XPERT-PRO diffractometer with Cu Kα radiation of wavelength λ = 1.544A°. The sample was scanned over the range from 20°- 80°. The XRD pattern obtained for the Al doped HBA crystal shown in **Figure 3**.The sharp peaks found in the spectra show good crystallinity of the grown single crystal. The observed 2ɵ and "d" values are presented in the **Table 1**.

***FTIR analysis***

FTIR spectrum of pure and AN doped 2HBA, and grown crystals were recorded on a SHIMADZU spectrophotometer in the range 400–4000 cm$^{-1}$ using a KBr pellet technique and compared. The presences of functional groups were confirmed by identifying absorption peaks in their characteristic regions. The broad band with 3peaks centered around 3368, 3034, and 2929cm$^{-1}$ are due to C-H stretching vibrations. The peaks around the region 863 to1358cm$^{-1}$ are due

to C-C stretching. The peaks at 1228 $cm^{-1}$ is due to C-N Stretching [5-7].**Figure 4** shows the FTIR spectrum of pure and Al doped HBA

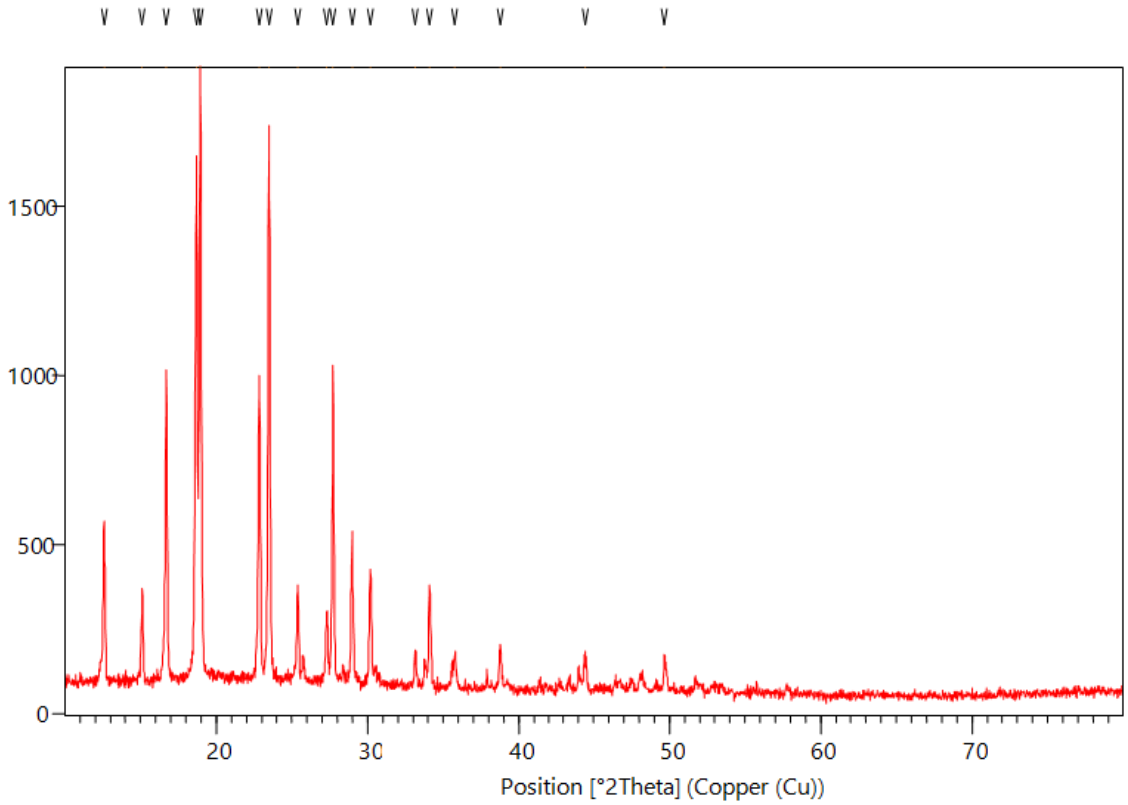


**Figure 3** Al Doped HBA.

**TABLE 1**

| S.NO | Pos. [°2Th.] | d-spacing [Å] | Rel. Int. [%] |
|---|---|---|---|
| 1 | 12.5868 | 7.03281 | 28.39 |
| 2 | 15.1140 | 5.86207 | 17.10 |
| 3 | 16.6998 | 5.30883 | 53.69 |
| 4 | 18.7177 | 4.74080 | 82.06 |
| 5 | 18.9642 | 4.67973 | 100.00 |
| 6 | 22.8216 | 3.89674 | 49.18 |
| 7 | 23.4884 | 3.78759 | 92.90 |
| 8 | 25.3904 | 3.50802 | 17.20 |
| 9 | 27.3085 | 3.26582 | 13.44 |
| 10 | 27.7141 | 3.21894 | 54.31 |
| 11 | 28.9902 | 3.08008 | 26.96 |
| 12 | 30.1851 | 2.96082 | 20.25 |
| 13 | 33.1572 | 2.70191 | 5.72 |
| 14 | 34.0959 | 2.62964 | 17.71 |
| 15 | 35.7316 | 2.51293 | 4.89 |
| 16 | 38.7450 | 2.32414 | 6.53 |
| 17 | 44.4642 | 2.03758 | 5.34 |
| 18 | 49.6714 | 1.83549 | 6.17 |

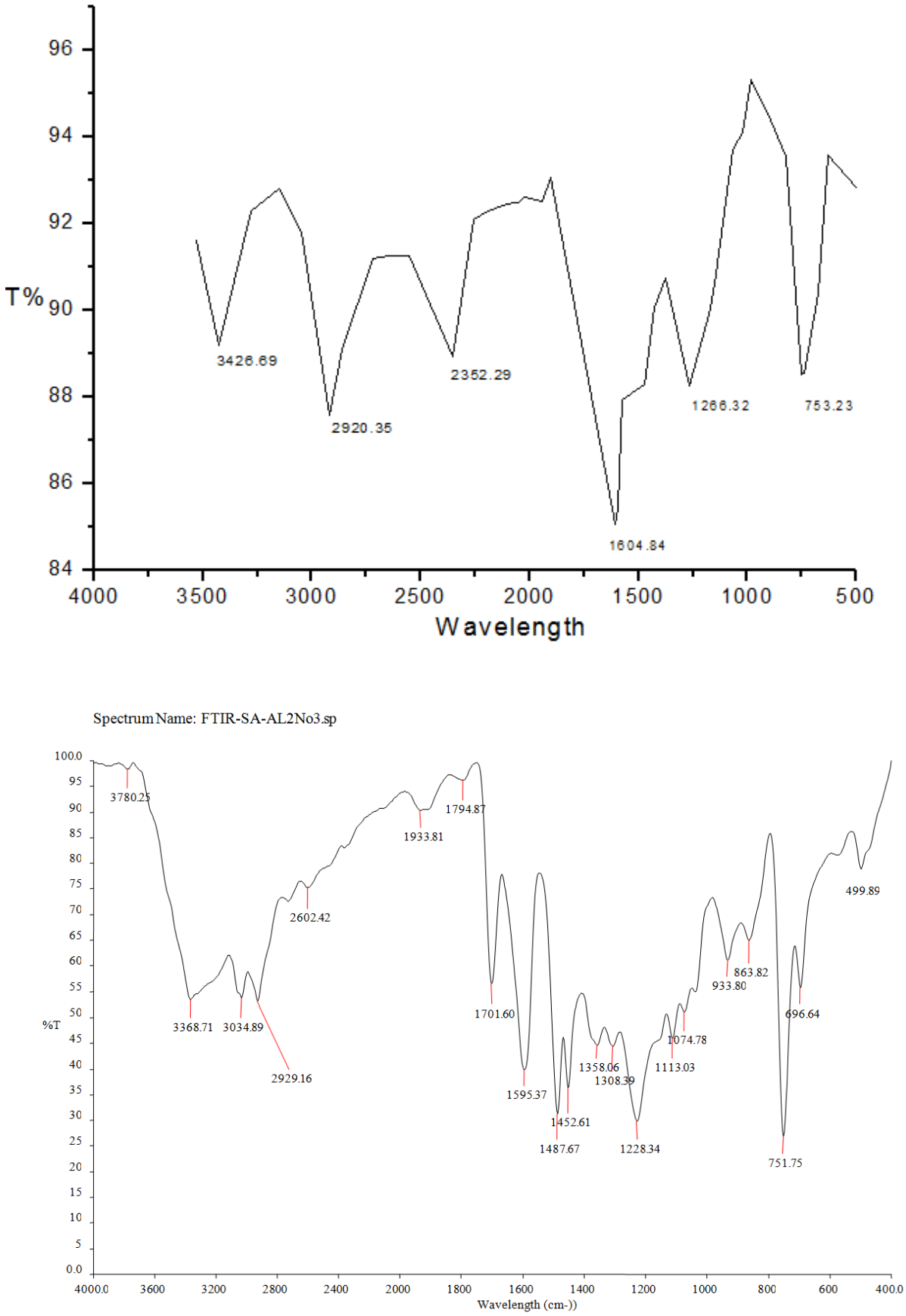


**Figure 4** FTIR spectra of (a) Pure HBA (b) Al Doped HBA.

**Table 2** FTIR Vibrational Assignment.

| Wavelength $cm^{-1}$ | | |
|---|---|---|
| **HBA** | **Al Doped HBA** | **Assignments** |
| 3426.69 | 3368.71 | Aromatic C-H Vibration |
| 2920.35 | 2929.26 | C=H Stretching |
| 1604.84 | 1701.60 | C=N stretching |
| 1471.75 | 1487.67 | C-H Def |
| 1266 | 1228.36 | C–N stretching vibration |
| 753 | 751.75 | C-H out of plane bending vibration |

***EDAX –Energy dispersive X –Ray spectroscopy***

EDAX is the Analytical technique which is used for the elemental analysis (or) chemical characterization of a sample. **Figure 5a** shows the EDAX analysis of the as received Al doped HBA sample and the presence of the elements Al, C and O is detected. The morphology of the sample which can be seen in Figure 5b as follows,

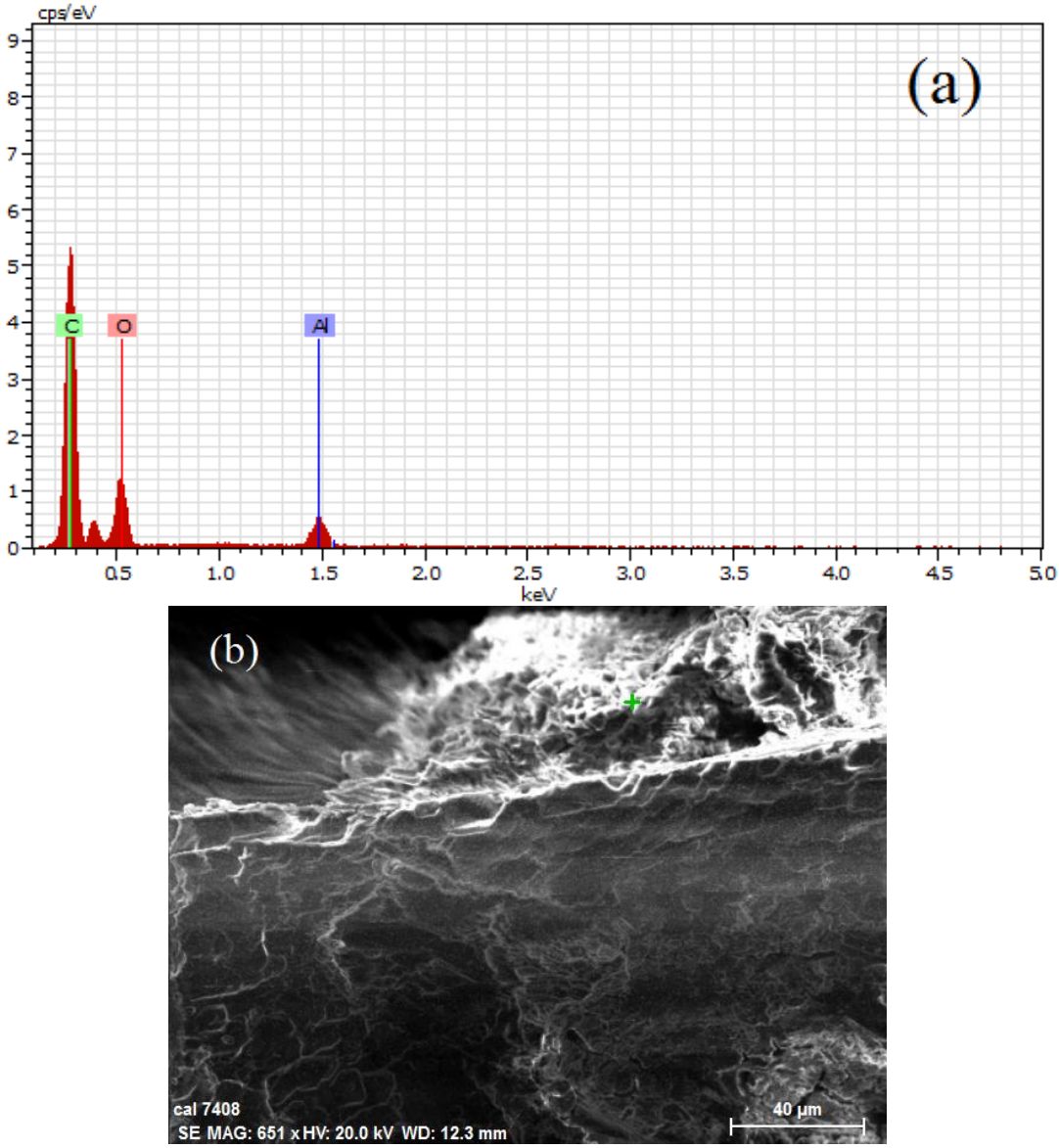


**Figure 5** EDAX Analysis of the Al doped HBA.

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Spectrum: sample 9760

El AN Series unn. C norm. C Atom. C Error (1 Sigma)
[wt.%] [wt.%] [at.%] [wt.%]
---------------------------------------------------
C 6 K-series 64.29 64.29 71.02 9.35
O 8 K-series 33.82 33.82 28.05 6.40
Al 13 K-series 1.89 1.89 0.93 0.15
---------------------------------------------------
Total: 100.00 100.00 100.00
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## UV – Visible study

The UV –Vis spectrum gives limited information about the structure if the materials of absorption of UV and Visible light involve the promotion of the electron in σ and Π orbital from the ground state to higher energy states. NLO material the transmission spectrum is very important because it has wide transparency window (9).The absorption spectrum of both pure and doped crystals were recorded in the wavelength range from 190 – 1100nm.The spectra are shown in **Figure 6**. It is clear from the spectrum that lower cut off wavelength is shifted by 20nm due to the dopant and the bandgap energies are calculated using the formula UV =hc /λ and equal to 3.97eV and 4.08 eV. for the pure and doped crystals respectively.

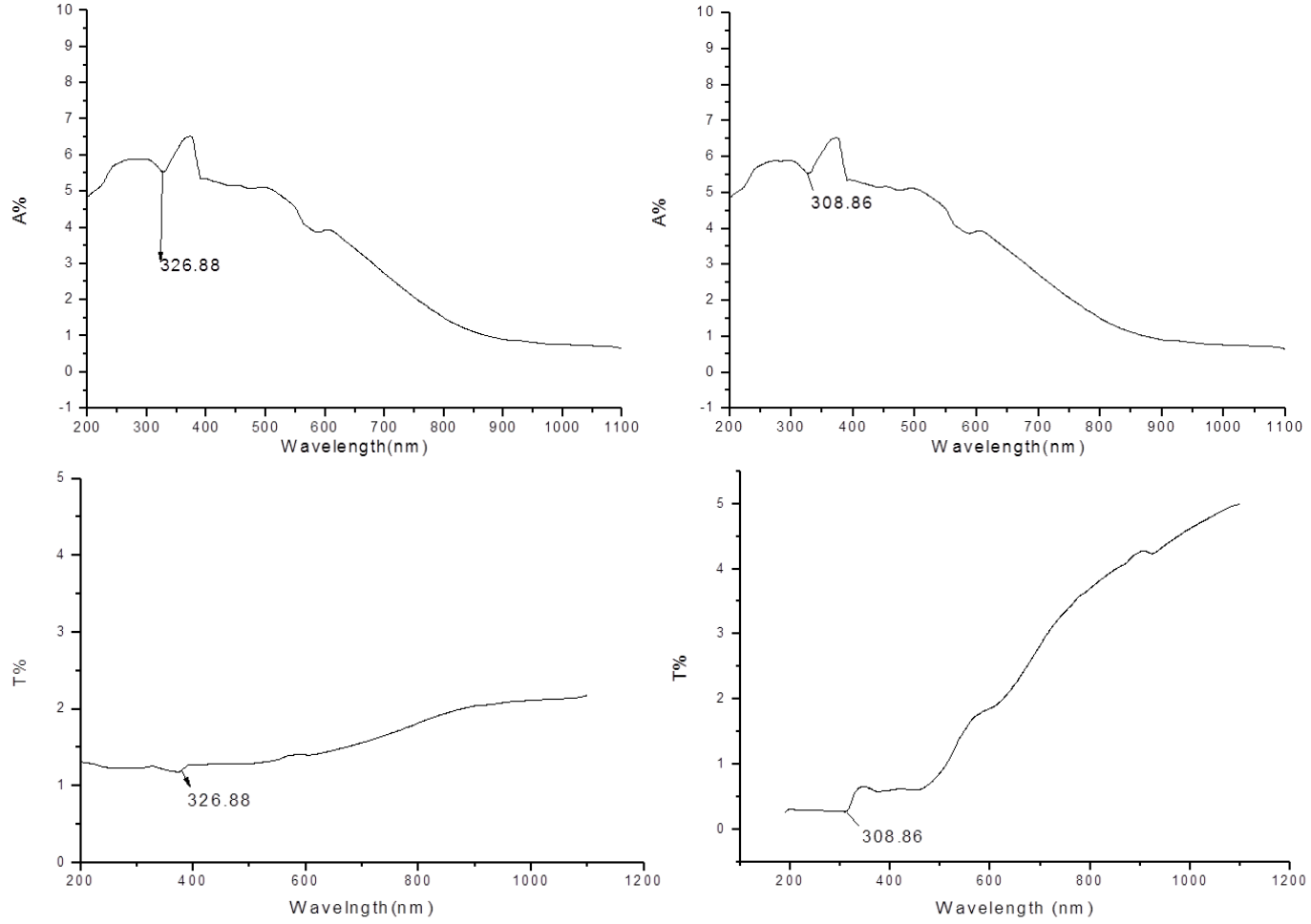


**Figure 6** UV Absorption and transmission spectra for pure and doped crystals.

## Micro hardness studies

Hardness is the one of the important properties to determine the plastic nature and strength of a material. Vickers micro hardness indentation test is used to characterize the hardness of the material. It is a non-destructive method to study the mechanical behavior of the material. It is a resistance against plastic deformation [10]. The selected surface of the grown crystals were polished, washed and dried. Hardness measurements were taken for applied loads varying from 25 to 100 gm keeping the indentation constant at 10sec. The hardness number was calculated using the relation $H_V = (1.8544) / (d^2)$ Kg/mm$^2$. Where $H_V$ is Vickers hardness number is applied load in Kg, d is the average diagonal length in mm of the indentation impression. The graph is plotted between hardness number ($H_V$) and applied load is shown in **Figure 7**. From the graph,it is found that hardness value increases with the increase of load which is in agreement with the normal indentation size effect (ISE)observed for other NLO crystals. The Meyers index number "n" estimated from the slope of the Figure 7 is 5.8 which indicates that the grown crystal belongs to soft material category [11]

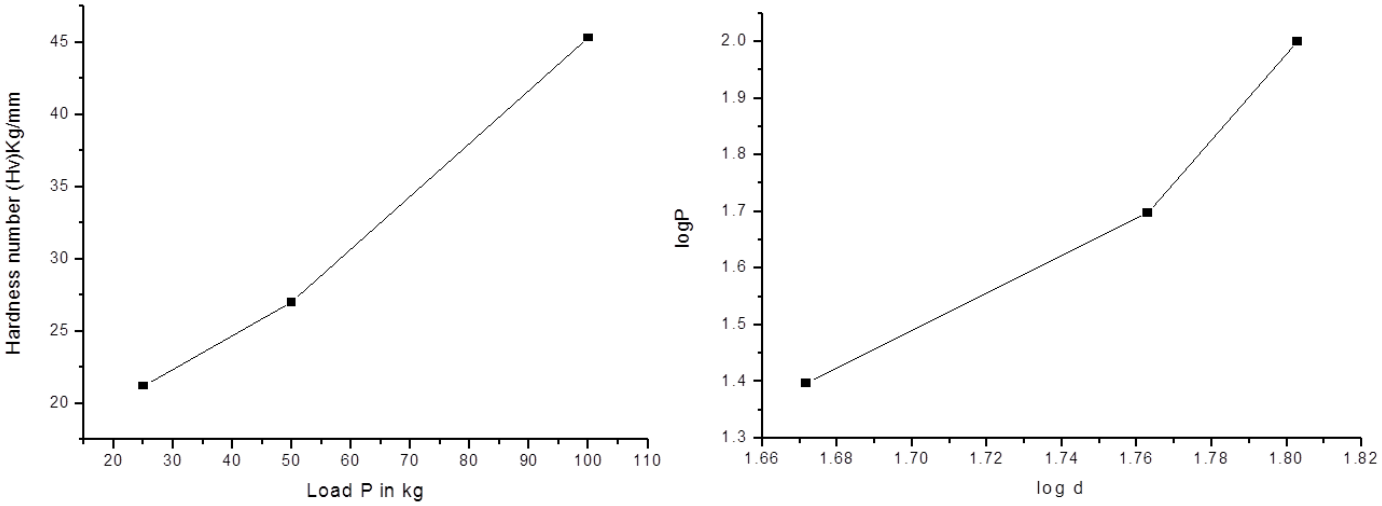


**Figure 7** Vickers Hardness test for pure and doped crystal.

## Second Harmonic Generation Efficiency

Second harmonic generation measurement was performed using Nd:YSAG laser of wavelength 1064nm,using Kurtz and Perry method. A relevant comparison was made on KDP with Al doped HBA. The reference material was also powdered and used for studies. The experimental samples reported an input pulse of 1Mj, the second harmonic generation at 95Mw for KDP and 77Mw for Al doped HBA. It is thus calculated that the SHG efficiency of the Al doped crystal in 0.8 times as that of KDP [12].

## Conclusion

Single crystals of Al doped HBA were successfully grown by slow evaporation Technique. The lattice parameters have been determined from the Single crystal XRD pattern. The Functional group of the compound have been identified by Fourier transform infra red spectra.UV-Vis –NIR Spectrum reveals that the crystal is transparent between 200nm-600nm and the band gap energy was determined as 4.024eV. SHG efficiency is 81%of that of standard KDP. The mechanical property was evaluated by Vickers micro hardness method.

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